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Harmon Engineering and Testing
Auburn, AL

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A STUDY TO EVALUATE AND IMPROVE EPA REFERENCE METHOD 16

by

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A modification to EPA Reference Method 16 was developed to eliminate known deficiencies in the analysis of total reduced sulfur (TRS) from stationary sources at kraft pulp mills. The modifications include: (1) The addition of a cold, citrate buffer gas scrubbing solution at the source, (2) The elimination of the need for a heated sample system and a dilution system, (3) Elimination of the need for two GC systems, (4) Changing the GC separation columns and valving to eliminate interference from CO_2, COS, and SO_2, (5) Finding a method for checking the linearity of the calibration curve. The proposed method was field evaluated by testing a lime kiln, a recovery boiler, and a smelt dissolving tank vent at a kraft pulp mill. The proposed method produced accurate results from each source.

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FORWARD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

The following investigation was conducted at the request of the Office of Air Quality Planning and Standards. A test method for the measurement of reduced sulfur compounds from kraft pulp mills, EPA Reference Method 16, was validated. The method was modified to eliminate known deficiencies. A scrubbing system was developed that removed interferences from sulfur dioxide, moisture condensate and alkaline particulate. The work also included studies of gas chromatographic techniques and procedures that will enable the analyst to measure the compounds of interest free from interferences from carbon dioxide and carbonyl sulfide and the necessity of using two gas chromatographic systems. The modified method was evaluated under realistic field conditions.

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ABSTRACT

A modification to EPA Reference Method 16 was developed to eliminate known deficiencies in the analysis of total reduced sulfur (TRS) from stationary sources at kraft pulp mills. The modifications include:

1. The addition of a cold, citrate buffer gas scrubbing solution at the source,
2. The elimination of the need for a heated sample system and a dilution system,
3. Elimination of the need for two GC systems,
4. Changing the GC separation columns and valving to eliminate interference from CO_2, COS, and SO_2,
5. Finding a method of checking the linearity of the calibration curve.

The proposed method was field evaluated by testing a lime kiln, a recovery boiler, and a smelt dissolving tank vent at a kraft pulp mill. The proposed method produced accurate results from each source.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

mL	-- milliliter
uL	-- microliter
ppm	-- parts per million
uV	-- microvolt
sec	-- second
cm	-- centimeter
°C	-- degrees celsius
mm	-- millimeter
psi	-- pounds per square inch
L	-- liter
nm	-- nanometer
ug	-- microgram
i.d.	-- internal diameter
o.d.	-- outside diameter
amps	-- amperes
std dev	-- standard deviation
RSD	-- relative standard deviation

SYMBOLS

H_2S	-- hydrogen sulfide
MeSH	-- methyl mercaptan
DMS	-- dimethyl sulfide
DMDS	-- dimethyl disulfide
GC	-- gas chromatograph
FPD	-- flame photometric detector
SO_2	-- sulfur dioxide
COS	-- carbonyl sulfide
Hg	-- mercury
CO_2	-- carbon dioxide
NCASI	-- National Council of the Paper Industry for Air and Stream Improvement
N_2	-- Nitrogen
O_2	-- oxygen
HE&T	-- Harmon Engineering & Testing
SwRI	-- Southwest Research Institute
HAI 601	-- Houston Atlas, Inc. Model 601 reference gas generator
FPD	-- flame photometric detector
CS_2	-- carbon disulfide

SECTION 1

INTRODUCTION

Reduced sulfur emissions at kraft pulp mills are measured using EPA Reference Method 16. The equipment to be used at the conditions were specified in the Federal Register 41, pages 42017-42020, September 24, 1976. The method was later modified to allow other separation columns and conditions to be used provided they met certain criteria (Federal Register 43, pages 7568-7598, February 23, 1978).

According to the published method, a sample of gas is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS). The method is applicable for the determination of the TRS compounds from emission sources at kraft pulp mills.

After field use the method was found to have several deficiencies that affect the accuracy and reproducibility of the results obtained. Some of those deficiencies are:

1. The method requires the use of two gas chromatographs and two recorders to analyze for the four reduced sulfur compounds.

2. The dilution system will not give reproducible dilutions in a field environment.

3. Carbon dioxide (CO_2) was found to elute with H_2S from the GC column and interfere with the determination of H_2S by a quenching action in the flame.

4. Carbonyl sulfide (COS) elutes from the GC column at the same time as H_2S.

5. Condensation of moisture within the system requires a totally heated system prior to dilution with air.

These deficiencies were noted by a number of researchers but the actual effect on the data collected was unknown.

This report presents a systematic evaluation of Method 16 and recommends modifications to the existing method. The following subtasks were completed:

1. Evaluate the known deficiencies and inaccuracies of the existing method of analysis.

2. Prepare a work plan for an evaluation study of the method.

3. Modify existing equipment and construct new equipment as required to eliminate all known deficiencies.

4. Modify the analytical procedure as required to ensure the collection of quality data.

5. Perform a field evaluation of the modified method at a kraft pulp mill.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study are based on a literature survey, a preliminary report by Southwest Research Institute (1), a report by NCASI (2), and laboratory and field evaluation of the techniques used to analyze for reduced sulfur compounds at kraft pulp mills. Harmon Engineering & Testing (HE&T) used its previous experience in TRS testing as a starting point for the method evaluation and development. The specific conclusions of this study are as follows:

1. A cold, citrate-buffer gas scrubbing solution located at the source eliminates:

   a. The need for heated sample lines (except) in environments where the ambient temperature is less than 35°F),

   b. The need for a heated dilution unit, and

   c. Interference from CO_2.

2. The dilution system given in Method 16 will not produce reproducible dilutions. A new system was designed that will produce reproducible dilutions.

3. A modified gas chromatographic system was developed that will separate all reduced sulfur compounds from each other and all known interferences at isothermal conditions.

4. Permeation tubes offer a convenient, precise, accurate means of field calibration of the GC system.

5. Aluminum cylinders of reduced sulfur compounds in nitrogen are stable over long periods of time if the concentrations are greater than 4 ppm.

6. A Houston Atlas, Inc. Model 601 Reference Gas Generator is useful in generating large volumes of standard gas in a field environment to check sample system TRS losses.

7. A Tracor Model 560 Gas Chromatograph with a Hall Electrolytic Detector did not prove satisfactory for field analysis of reduced sulfur compounds.

8. It is possible to obtain more than an 80 percent recovery of a 5 ppm mixture of H_2S in air through a modified analytical system.

9. Significant losses of TRS are not observed in an in-stack glass-wool filter.

10. Carbonyl sulfide (COS) is present in some kraft pulp mill emission sources in concentrations that are related to the oxygen content of the source gas.

As a result of this study, it is recommended that EPA Reference Method 16 be modified to eliminate the known deficiencies and to simplify the analyses. The recommended modifications to the method are given in a new version of Method 16 included as an appendix to this report. This proposed method incorporates all conclusions of this study and describes an example system developed in the study.

SECTION 3

EXPERIMENTAL PROCEDURES

This section describes the equipment used in the field evaluation at the completion of the study. Other equipment used throughout the study was not as reliable as these items.

GAS CHROMATOGRAPH

A Tracor Model 250H Gas Chromatograph equipped with a Melpar flame photometric detector (FPD) was used for all chromatographic separations and detections. The peak heights were measured on a Westronics Strip Chart Recorder, and a Laboratory Data Control Model 308 electronic integrator was used to determine peak areas. The gas chromatograph was modified by the addition of a multiport switching valve and digital valve interfaces. The valve switching sequence was controlled by the electronic integrator through the digital valve interfaces. Manual operation of the multiport valves was also possible.

GC COLUMNS

Two columns were required for efficient separation - a 4.8' x 1/8" o.d. Teflon column packed with Carbopack B HT 100 was used for the primary separation and a 3' x 1/8" o.d. Teflon column packed with 9.5 percent polyphenyl ether and 0.5 percent orthophosphoric acid on 40/60 mesh Teflon beads were used as a post column. These columns are commercially available from Alltech Associates, Arlington Heights, Illinois.

SAMPLE VALVES

The 4 port and 10 port switching valves were constructed from Hastalloy C. These air actuated valves were supplied by Valco Instruments, Houston, Texas.

CALIBRATION SYSTEM

O'Keeffe type permeation tubes, containing H_2S, MeSH, DMS, DMDS, were purchased from Metronics, Inc., Palo Alto, California. The permeation rates were certified by the vendor and verified upon arrival. A Metronics Model 220F Dynacalibrator was used to maintain a constant temperature to determine the emission rate. The same instrument was used to establish the standard gases throughout the study.

DILUTION SYSTEM

The dilution system was constructed by HE&T. All parts of construction were stainless steel, Teflon or glass. Magnehelic gauges purchased from Dwyer Instruments, Inc., Michigan City, Indiana, were used to monitor pressures and vacuums within the system. Rotameters were purchased from Matheson Instruments, Horsham, Pennsylvania. Nupro valves and Swagelok fittings were used throughout the dilution apparatus.

SULFUR DIOXIDE SCRUBBER

The scrubber system was constructed by HE&T from Teflon components. The Teflon containers from the scrubber were purchased from Savillex Corporation, Minnetonka, Minnesota.

STANDARD GAS GENERATOR

Standard concentrations of H_2S for checking recovery throughout the system were generated with a Houston Atlas, Inc. Model 601 (HAI 601) PPM gas generator. The instrument was modified after purchase by HE&T to provide the needed dilutions.

CALIBRATION GAS CYLINDERS

Calibration gases were purchased from Scott Speciality Gases, Plumsteadville, Pennsylvania. Scott Acublend calibration gases were stored in treated aluminum cylinders.

SECTION 4

RESULTS AND DISCUSSION

Hamil and Swynnerton (1) performed a laboratory study of EPA Reference Method 15 and 16 to determine the applicability of the existing method for analysis of TRS. Their work is summarized below:

1. The flame photometric detector (FPD) possessed the required sensitivity and selectivity but it suffers from a nonlinear response and a limited dynamic range in the sulfur mode. Its signal is also quenched by the presence of nonsulfur containing compounds which may coelute with the reduced sulfur compounds. The calculated quadratic response of the detector to sulfur containing species was not valid.

2. Isothermal separation of the four reduced sulfur compounds of Method 16 could not be obtained without the use of backflush techniques or temperature programming. Temperature programming was determined to be unacceptable due to the lengthy analysis time and the leak problems caused by the "cold flow" of Teflon columns and fittings at elevated temperatures.

3. Permeation tubes of the O'Keeffe type containing H_2S, MeSH, DMS, and DMDS were found to permeate at a constant rate over a three month period, one month after date of purchase. Experimentally determined rates were, in general, in fair agreement with thos certified by the vendor. It was recommended that vendor certified permeation rates be checked experimentally by the purchaser at the conditions of use.

4. Aluminum cylinders containing low ppm TRS concentrations were relatively stable over a period of time. Some slight loss was seen in H_2S concentrations of less than 5 ppm, but no apparent change was observed in the other compounds after four months.

5. All attempts to build a workable dilution system using the Kohmyhr A-150 pumps failed. When a back pressure of more than one to two centimeters Hg was encountered by the pump, it leaked. The leak rate was dependent on the back pressure and the dilution factor could not be accurately determined.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted a study on the evaluation of several scrubbing solutions to remove SO_2 from a gas stream without affecting the TRS (2). They found that a citric acid/potassium citrate buffer at pH 5.6 would remove the SO_2 and yet leave the reduced sulfur compounds unaffected. This scrubbing solution was incorporated into Method 16 to remove the SO_2 prior to analysis by the GC.

Previous experience by HE&T personnel in performing TRS analysis using Method 16 in a field environment indicated the following problems:

1. The dilution system specified in Method 16 would not yield accurate, reproducible dilutions. The system would leak with the changing of the back pressure.

2. Excessive losses of hydrogen sulfide were experienced through the sampling systemm after a period of time. The losses appeared to be coming as a result of the collection of particulate matter within the probe and sample line.

3. Carbonyl sulfide (COS) coelutes with hydrogen sulfide when the specified column was used. On sources with amounts of COS present, the H_2S concentration would appear much too high.

4. Carbon dioxide would coelute with hydrogen sulfide causing a reduced signal from H_2S. The quenching effect would be observed primarily from lime kilns where the CO_2 concentration could not be reduced by dilution to the point that it would not affect the results.

5. The required reproducibility between for serial could not be achieved on a routine basis using the existing system.

Based on the previous experience of HE&T and the other results described above, this study's goal was to obtain an analytical system that would correct the deficiencies of the existing system and simplify the analysis as much as possible. Figure 1 shows a schematic drawing of the analytical system developed for TRS analysis. The following paragraphs will discuss each component.

DESIGN OF THE SO_2 SCRUBBER

Figure 2 presents a schematic drawing of the probe and SO_2 scrubber assembly. On the basis of the work of the NCASI (2), the best place to locate the scrubber would be at the source. By locating the SO_2 scrubber in an ice bath, the moisture would be removed from the sample stream to allow the transport of a clean dry sample. A Teflon container filled with glass wool was located as an in-stack filter to remove particulate matter immediately after the sample is introduced into the probe. The sample line was heated until just above the first impinger. Rapid cooling and condensation of the water takes place within the first impinger.

Figure 3 shows a drawing of the probe and filter assembly that was used to evaluate sample losses within the glass wool filter. The standard gas could be introduced either before or after the filter to determine the relative losses. The sample line was constructed of either Teflon tubing or Teflon lined stainless steel tubing to provide an inert wall for contact with the TRS compounds. As shown in later sections, significant losses of hydrogen sulfide were not experienced when passing through this glass wool filter.

Due to the extensive evaluation of the SO_2 scrubbing by the NCASI (2) no additional evaluations were performed on the scrubbing solutions. Locating the SO_2 scrubbers in an ice bath at the source eliminates the need for long heated sample line and the requirement to dilute the sample gas with air to reduce the dew point. When the impingers were immersed in an ice bath, the gas temperature within the last impinger was always less than $5^{o}C$. At this temperature, the sample gas will contain less than 1 percent moisture.

DILUTION SYSTEM

Figure 4 shows a schematic drawing of the dilution system designed and constructed to provide more accurate and reproducible dilutions. Since the incoming gas was dry, there was no requirement to heat the system. The system was maintained at ambient temperature and pressure. The system operated under a normal vacuum of 1.5-2.5 psi. Due to the constrictions within the GC sample loop, the pressure of the sample within the sample loop was dependent not only on the inlet pressure but also on the flow rate of the gas through the sample loop. It was extremely important to maintain a constant pressure within the sampling system.

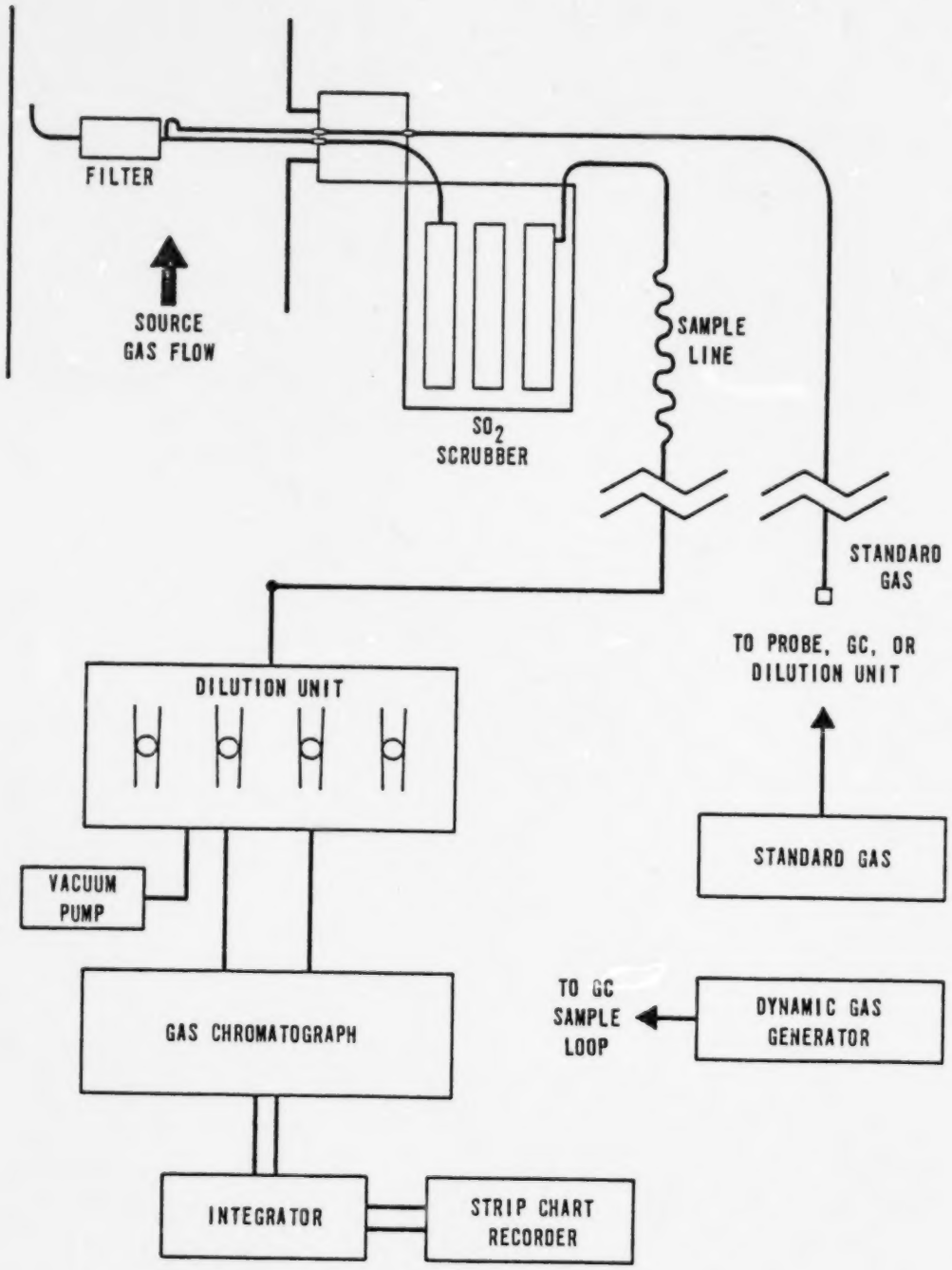


Figure 1. Schematic drawing of the TRS analytical system.

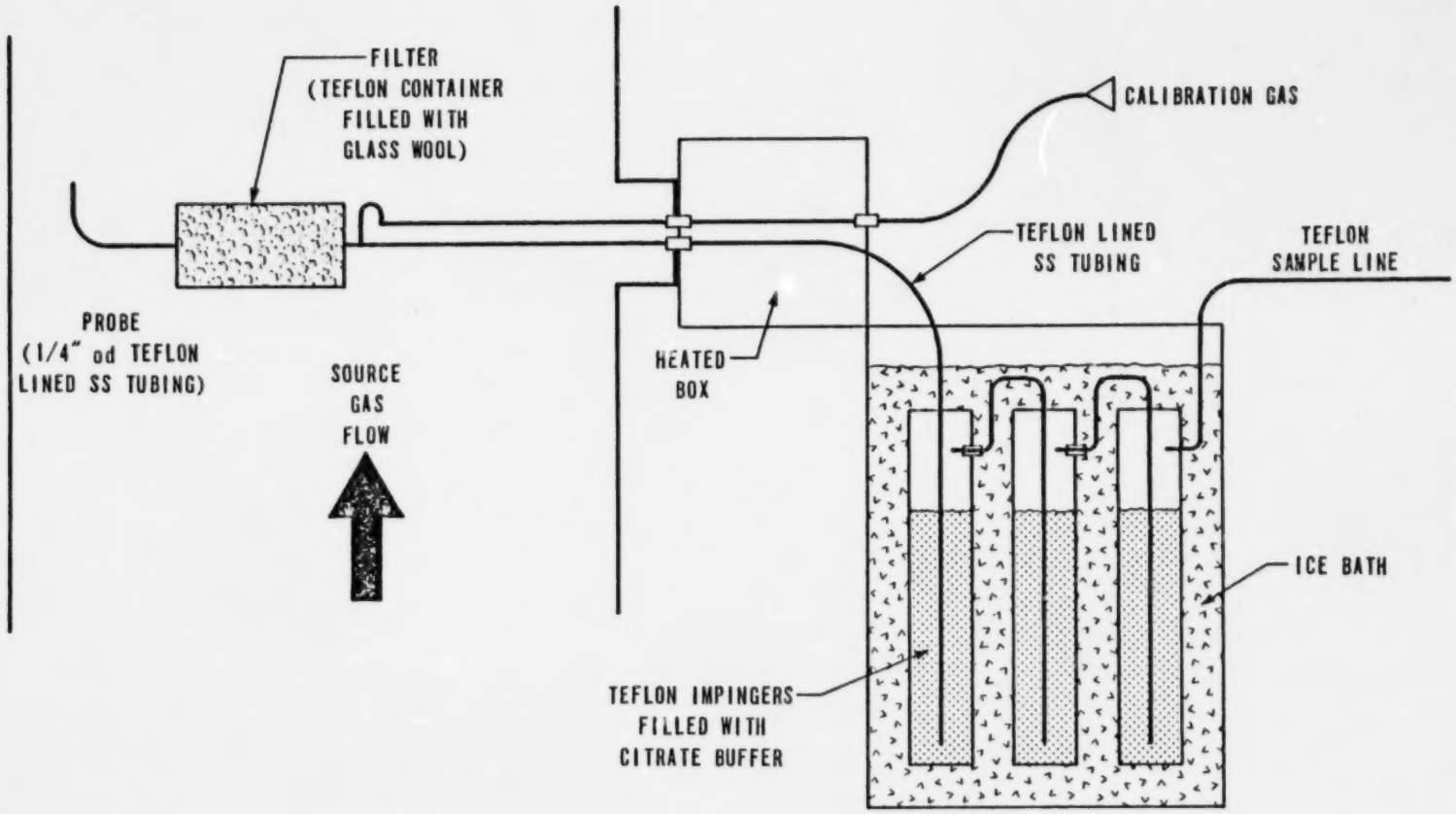


Figure 2. Probe/SO_2 scrubber assembly.

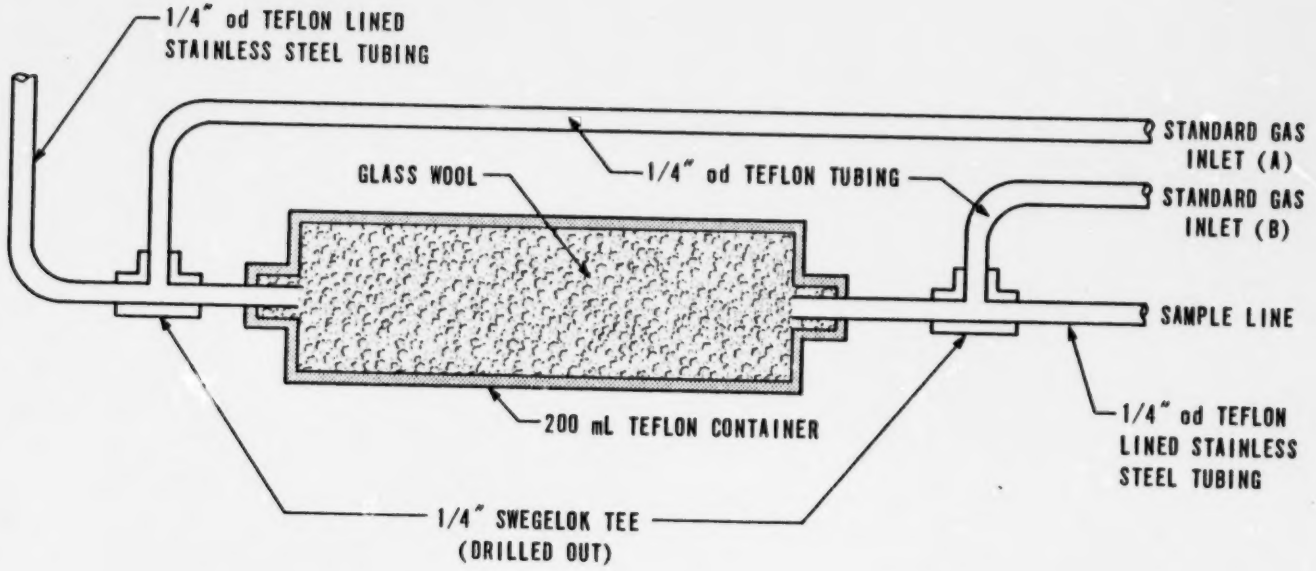


Figure 3. Probe and filter assembly to allow the introduction of standard gas before and after the filter.

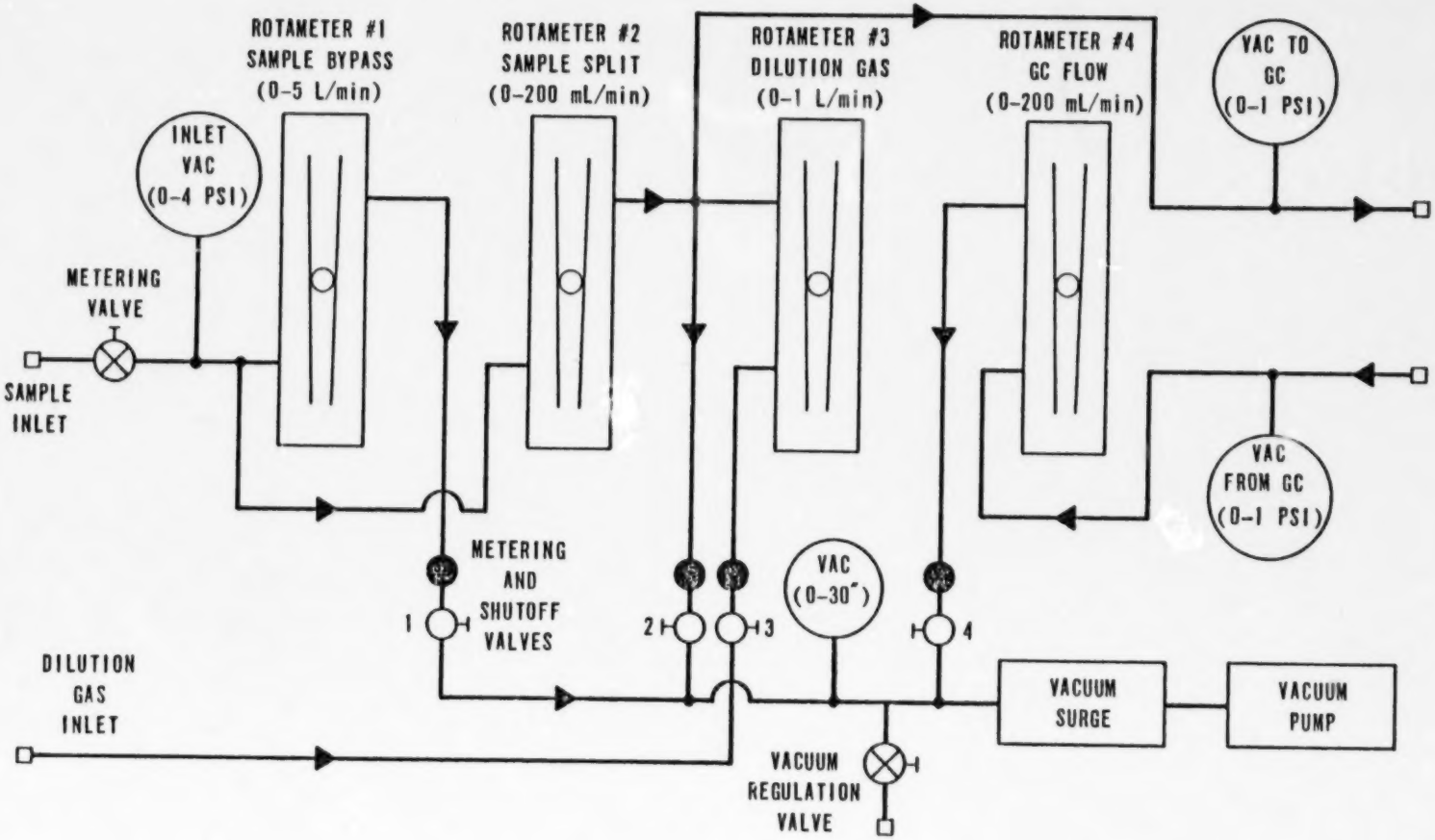


Figure 4. Schematic drawing of dilution system.

Table 1 shows a comparison of the calculated dilutions and those actually obtained with the system. This table indicates that it was not possible to actually calculate the desired dilution factor. The rotameter settings and the pressure gauges only give the approximate dilution factor to be used. The rotameters were all calibrated at the used pressure but the calculated value still varies due to slight variations in the flow through the rotameters.

Table 2 shows the consistency obtained for the dilution unit once it is placed into operation. The values in Table 2 were obtained by running the system over a long period of time without making any changes in the pressure or flow settings of the system. It is apparent from these two tables that the actual dilution must be recalculated each time any changes are made in the flow or pressure settings.

GAS CHROMATOGRAPHIC SYSTEM

Figure 5 shows a schematic drawing of the gas chromatograph used for the separations. The Tracor Model 250H was modified to incorporate the addition of a 4 port valve. The 10 port valve was used to inject the sample and backflush the precolumn. The 4 port valve was used to reverse the flow in separation column #1 to enable the separation of all four reduced sulfur compounds at isothermal conditions.

The volume of the sample loop was changed by varying the length of 1/8" o.d. Teflon tube. The precolumn was a 1' length of Teflon tubing packed with polyphenyl ether and phosphoric acid on Teflon beads. The precolumn was used to protect the separation columns from contamination by higher molecular weight sulfur compounds. Separation column #1 was a 4.5' x 1/8" o.d. Teflon tube packed with Carbosorb B HT 100. Separation column #2 was a 3' length of 1/8" o.d. Teflon tubing packed with polyphenyl ether and phosphoric acid on Teflon beads and was used to prevent the flame blow-out during valve switching.

The multiport valves were air actuated by means of solenoid valve. Since the time of valve switching is critical to the separation times, the valves were controlled by means of a digital valve interface which was timed from the electronic integrator.

Figure 6 shows a sample chromatogram obtained from the system for the analysis of the four reduced sulfur compounds designated as TRS. The instrument conditions and concentrations of the compounds are given on the chromatogram. All four compounds were eluted in less than five minutes. The low carrier flow during the first 59 seconds of the run is necessary to obtain separation of CO_2 and air from the H_2S. The CO_2 elutes in approximately 50 seconds.

TABLE 1. COMPARISON OF CALCULATED AND ACTUAL DILUTIONS

(1) H_2S concentration input (ppm)	(2) H_2S concentration measured (ppm)	(3) Sample flow (mL/min)	(4) Dilution air flow (mL/min)	(5) Calculated dilution factor	(6) Actual dilution factor	(7) Variation from calculated (%)
6.6	5.96	50	0	1.16	1.21	+ 4.3
11.9	5.96	50	50	2.32	2.00	-13.8
23.8	5.31	50	150	4.64	4.48	- 3.6
35.7	4.92	50	250	6.96	7.26	+ 4.3
59.5	5.06	50	450	11.6	11.8	+ 1.7
5.5	4.76	50	0	1.16	1.16	0
5.5	2.00	50	50	2.32	2.75	+18.5
10.9	4.32	50	50	2.32	2.52	+ 8.6
21.8	4.24	50	150	4.64	5.14	+10.8
21.8	2.86	50	250	6.96	7.62	+ 9.5
5.6	4.77	50	0	1.16	1.17	+ 0.9
5.6	1.51	50	100	3.48	3.71	+ 6.6
11.2	2.80	50	100	3.48	4.00	+14.9
22.3	3.50	50	200	5.80	6.37	+ 9.8

(1) The known H_2S trace gas was generated with the HAI 601 by measuring flow and injection rate. Instrument was calibrated daily by measuring concentration with GC.

(2) H_2S concentration was that measured by GC after dilution. The vacuum in the dilution system was 2.0 psi. The calculated dilution due to this pressure was 1.16.

(3) Sample flow was the apparent flow as measured by the #2 rotameter.

(4) Dilution air flow was the apparent flow as measured by the #3 rotameter.

(5) The calculated dilution was obtained by the formula:

$$1.16 \times \frac{\text{Sample flow + dilution air flow}}{\text{Sample flow}}$$

(6) The actual dilution factor was calculated from the formula:

$$\frac{H_2S \text{ input concentration}}{H_2S \text{ measured concentration}}$$

(7) The percentage variation indicates the deviation of the observed values from the calculated values.

TABLE 2. VARIATION IN DILUTION FACTOR WITH RESPECT TO TIME

Time	Input H_2S concentration (ppm)	Measured H_2S concentration (ppm)	Calculated dilution factor	Measured dilution factor
1400	16.2	4.17	3.39	3.88
1600	16.4	4.31	3.42	3.81
2000	16.3	4.23	3.42	3.85
2145	16.7	4.31	3.42	3.87
Mean				3.85
RSD (%)				0.8

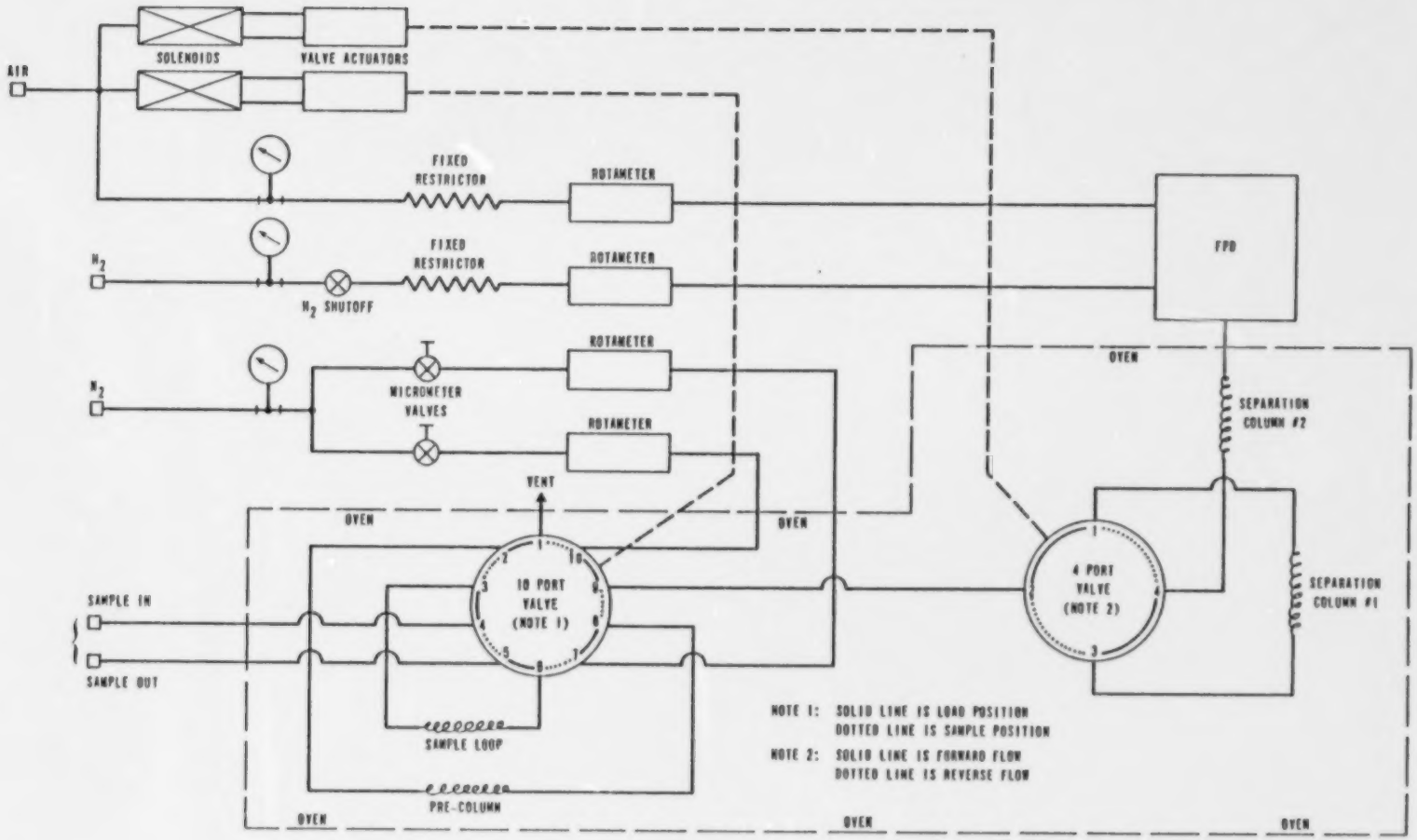


Figure 5. Schematic drawing of gas chromatograph.

SAMPLE SIZE = 1.4 mL

CARRIER (1) FLOW = 29 mL/min N_2

CARRIER (2) FLOW = 70 mL/min N_2

OXIDANT FLOW = 73 mL/min AIR

FUEL FLOW = 48 mL/min H_2

COLUMN TEMPERATURE = 65°C

DETECTOR TEMPERATURE = 125°C

EVENT 1 (INJECT) = 0 sec

EVENT 2 (STOP INJECT) = 59 sec

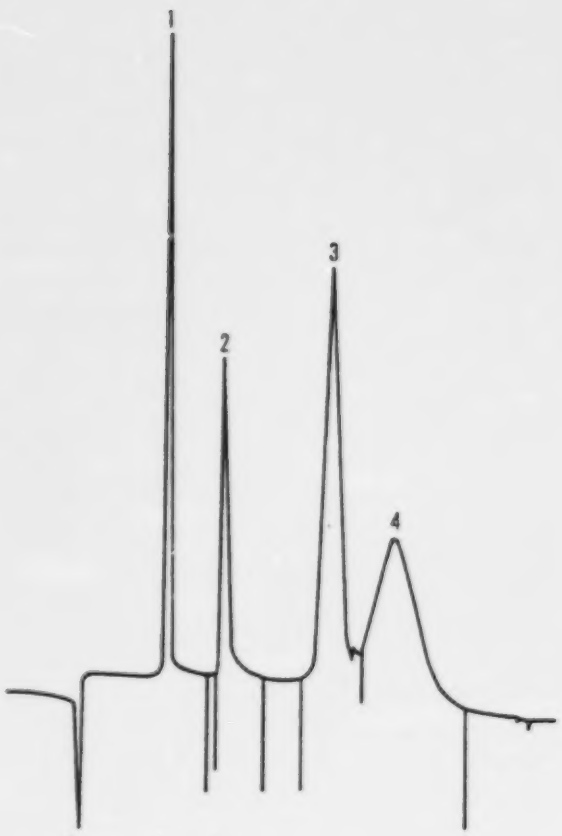
EVENT 3 (REVERSE FLOW) = 108 sec

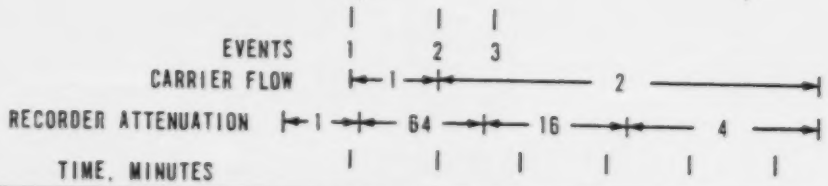
EVENT 4 (FORWARD FLOW) = 327 sec

CHART SPEED = 12.6 mm/min

INPUT ATTENUATION = 10^{-11} amps

OUTPUT ATTENUATION = 2





	COMPOUNDS	RETENTION TIME (sec)	CONCENTRATION (ppm)	AREA (μv-sec/16)	RETENTION RATIO
1	H_2S	66	3.4	5990	1.00
2	MeSH	106	4.3	4750	1.61
3	DMS	184	3.9	3509	2.79
4	DMDS	230	3.9	463	3.48

Figure 6. Chromatogram of H_2S, MeSH, DMS, and DMDS.

Table 3 shows the effect of CO_2 on the detector response to H_2S. Note that the response to the H_2S was greater when CO_2 was present. This should not be the case; the variation in peak areas observed was strictly a variation rather than a true effect due to the presence of CO_2. Carbon dioxide does have a desensitizing effect on the flame photometric detector. It was observed during the project that, if the CO_2 elution time was not separated from the H_2S by several seconds, a reduced sensitivity of H_2S results. Using the specified GC conditions, CO_2 did not affect the response of the GC to the TRS compounds.

Even though the SO_2 scrubber effectively removes SO_2 from the sample gas, it was desirable to show the retention time of SO_2 at the GC conditions. Figure 7 shows a chromatogram of H_2S, SO_2, and methyl mercaptan. Even if the SO_2 scrubber were not totally effective, the SO_2 would not interfere with the determination of the reduced sulfur compounds.

Carbonyl sulfide may be positive interference to the analysis of TRS. COS is not considered odoriferous and, therefore, should not be considered in the calculation of TRS. Figure 8 shows a chromatogram of a sample containing H_2S, COS, and methyl mercaptan. The COS elutes beteewn H_2S and methyl mercaptan so that, if it were present in a source, it would not interfere with the determination of TRS.

Many times the concentration of reduced sulfur compounds at existing sources will be out of the linear calibration curve prepared for the instrument. It then becomes advantageous to calibrate at a lower concentration and then to analyze at a much higher level. It was possible to extend the calibration range by using sample loops of different volumes. Table 4 indicates the effect of changing sample loop volume on the calibration curve slope and Y-intercept. The calculated volume of each sample loop was determined by multiplying the tubing length by the i.d. area. The response from the 1.4 mL sample loop should be exactly five times that of the 0.28 mL sample loop. By comparing the areas, the area obtained from a 1.0 part per million standard analyzed with the 1.4 mL sample loop should be exactly the same as a 5.0 ppm sample analyzed with the 0.28 mL sample loop. As is observed from the table, this was the case within the variation of the method. The best way to obtain the volume of each sample loop in relation to others was not to calculate the volume, but rather to measure it by calibration.

TABLE 3. EFFECT OF CO_2 ON FPD RESPONSE TO H_2S[1]

H_2S concentration (ppm)		Peak areas (uV-sec) air	Peak areas (uV-sec) 10% CO_2	Difference in mean (%)
5.0	Area (mean, uV-sec	28058	28212	0.5
	Std deviation, uV-sec	1108	669	
	Std deviation, %	3.9	2.4	
2.5	Area (mean), uV-sec	6876	7077	2.9
	Std deviation, uV-sec	136	151	
	Std deviation, %	2.0	2.1	
1.2	Area (mean), uV-sec	1888	2013	6.6
	Std deviation, uV-sec	153	100	
	Std deviation, %	8.1	5.0	

(1) H_2S gas was generated using HAI 601. Diluent was either reconstituted breathing air or 10% CO_2 in nitrogen. Multiple injects were analyzed at each concentration to determine the deviation due to repetitive analyses.

SAMPLE SIZE = 1.4 mL

CARRIER (1) FLOW = 29 mL/min N_2

CARRIER (2) FLOW = 70 mL/min N_2

OXIDANT FLOW = 73 mL/min AIR

FUEL FLOW = 48 mL/min H_2

COLUMN TEMPERATURE = 65°C

DETECTOR TEMPERATURE = 125°C

EVENT 1 (INJECT) = 0 sec

EVENT 2 (STOP INJECT) = 59 sec

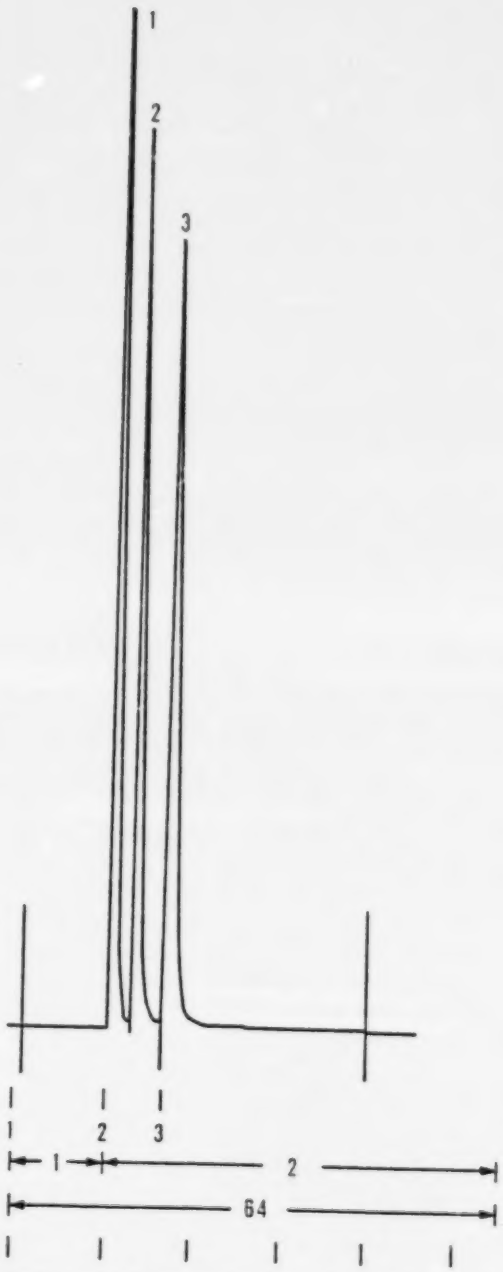
EVENT 3 (REVERSE FLOW) = 108 sec

EVENT 4 (FORWARD FLOW) = 327 sec

CHART SPEED = 12.6 mm/min

INPUT ATTENUATION = 10^{-11} amps

OUTPUT ATTENUATION = 2



	COMPOUNDS	RETENTION TIME (sec)	CONCENTRATION (ppm)	AREA (μv-sec/16)	RETENTION RATIO
1	H_2S	66	5.1	18008	1.00
2	SO_2	82	5.1	16379	1.24
3	MeSH	106	7.6	21152	1.61

Figure 7. Chromatogram of H_2S, SO_2, and MeSH.

SAMPLE SIZE = 1.4 mL

CARRIER (1) FLOW = 29 mL/min N_2

CARRIER (2) FLOW = 70 mL/min N_2

OXIDANT FLOW = 73 mL/min AIR

FUEL FLOW = 48 mL/min H_2

COLUMN TEMPERATURE = 65°C

DETECTOR TEMPERATURE = 125°C

EVENT 1 (INJECT) = 0 sec

EVENT 2 (STOP INJECT) = 59 sec

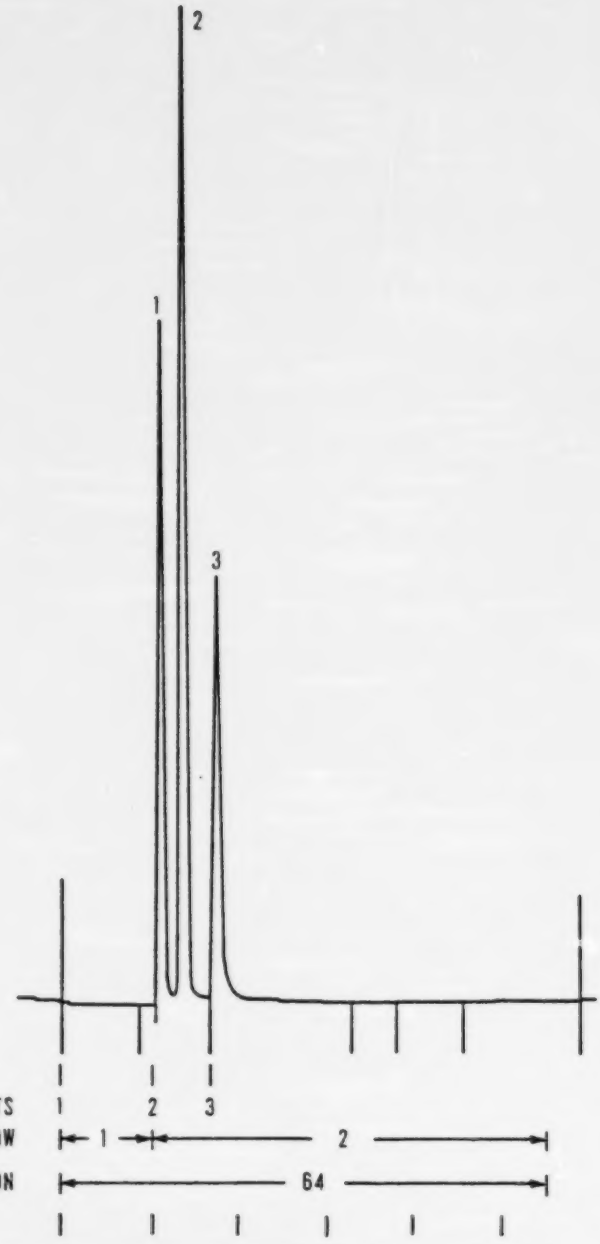
EVENT 3 (REVERSE FLOW) = 108 sec

EVENT 4 (FORWARD FLOW) = 327 sec

CHART SPEED = 12.6 mm/min

INPUT ATTENUATION = 10^{-11} amps

OUTPUT ATTENUATION = 2



	COMPOUNDS	RETENTION TIME (sec)	CONCENTRATION (ppm)	AREA (μv-sec/16)	RETENTION RATIO
1	H_2S	66	3.9	10173	1.00
2	COS	80	5.3	19187	1.21
3	MeSH	109	5.8	12150	1.61

Figure 8. Chromatogram of H_2S, COS, amd MeSH.

TABLE 4. H_2S CALIBRATION DATA AT TWO SAMPLE VOLUMES(1)

Calculated volume (mL)	Concentration (ppm)	Peak area (uV-sec) / 16	RDS (%)	Slope	Y-intercept
1.4	2.0	2102	7.8		
1.4	1.5	1263	6.1	1.82	597
1.4	1.0	595	4.2		
0.28	10.0	2101	8.4		
0.28	7.5	1232	8.2	1.91	5.62
0.28	5.0	560	6.8		

(1) Calculated sample loop volume
Difference in slope = 4.7%
Difference in intercept = 6.2%

The concentration and peak areas were plotted according to the equation:

$$Y = AX^B$$

where:

Y = peak area
X = concentration
A = Y-intercept
B = slope of line

GC CALIBRATION

Calibration of the GC was performed using gravimetrically calibrated permeation devices. The emission rates of the devices were certified by the vendor prior to shipment. The permeation rates of the devices used were:

COMPOUND NAME	PERMEATION RATE
H_2S	300 ng/min ± 5%
MeSH	540 ng/min ± 2%
DMS	655 ng/min ± 2%
DMDS	980 ng/min ± 3%

Each permeation device was certified and used at 50°C.

The permeation tubes were maintained at a constant temperature of ±0.1°C using a Metronics Model 220F Dynacalibrator. Figure 9 shows a schematic drawing of this device. The permeation tube chamber is held at a constant temperature by being enclosed in an aluminum block, which temperature is electronically held constant. For the purposes of this study, the bypass gas was not required. All calibration concentrations were generated by using gas flows ranging from 30-800 mL per minute.

The permeation rates were selected to allow the preparation of the calibration curve for each compound using the same gas flows. Figure 10 graphically shows calibration curves for each of the reduced sulfur compounds. Note that the slope for each of the compounds was nearly the same, but the instrument sensitivity varied from compound to compound. The low DMDS sensitivity was due to the longer retention time and the broad peak obtained.

Table 5 presents the data used to prepare the calibration curves shown in Figure 10. A linear least square best fit of the data was made using the equation:

$$Y = aX^b$$

To measure the fit of the data, after each curve was calculated, the average area for each given concentration was plotted on the curve and the calculated concentration for that point was obtained. This calculated concentration was then compared to the known concentration. As can be seen from the data, the points are extremely linear for this series of curves.

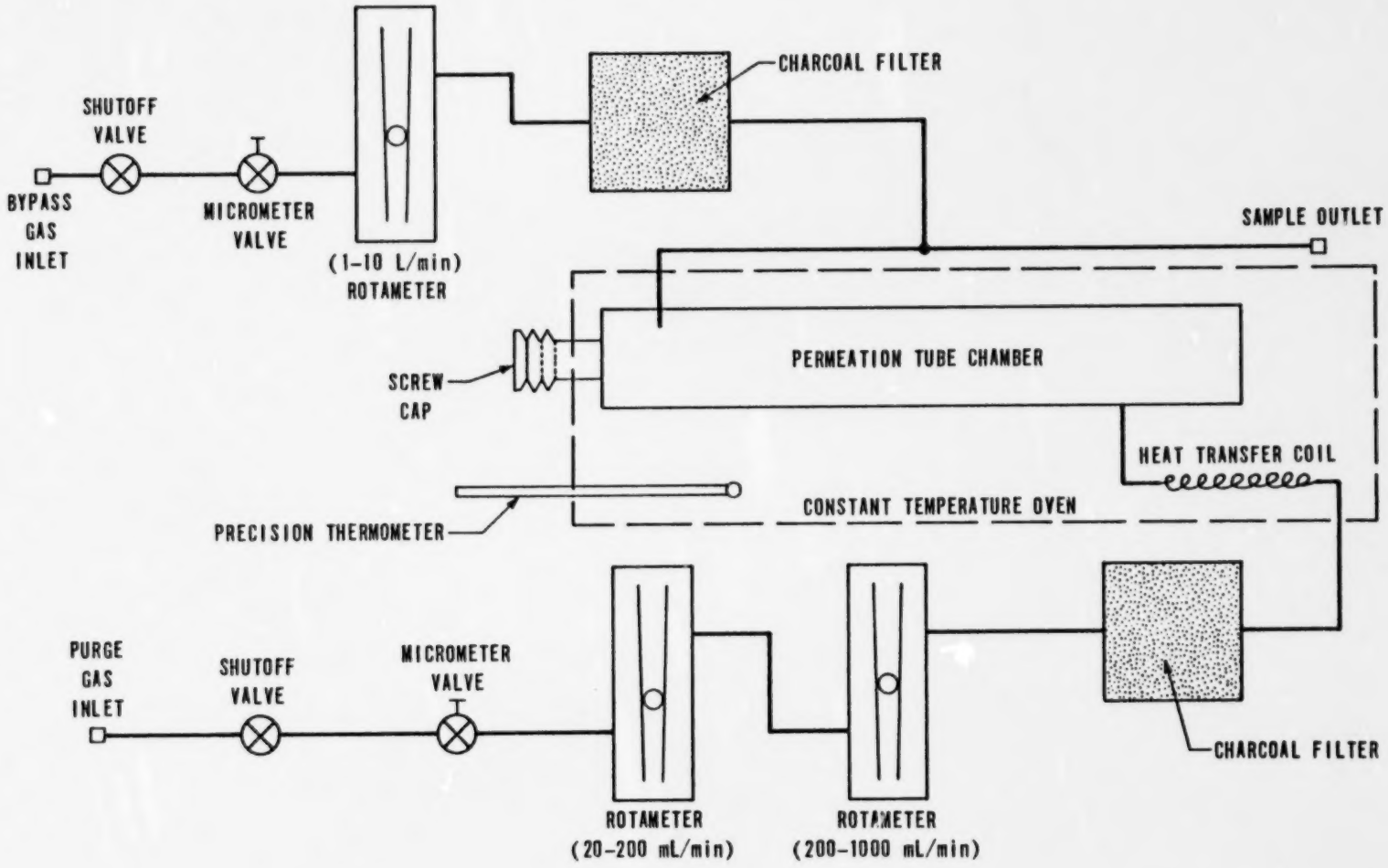


Figure 9. Schematic drawing of Metronics Model 220F dynacalibrator.

TABLE 5. CALIBRATION DATA FOR H_2S, MeSH, DMS, AND DMDS

Compound	H_2S	MeSH	DMS	DMDS
Permeation rate (uL/min)	216	275	255	255
Retention time (sec)	70	110	287	235

Permeation flow rate (mL/min)	Compound	Known concentration (ppm)	Area (uV-sec) 1	2	3	Average
64.5	H_2S	3.35	5990	5861	5959	5933
	MeSH	4.26	4750	4789	4730	4756
	DMS	3.95	3509	3426	3886	3607
	DMDS	3.95	463	490	544	499
136	H_2S	1.58	1408	1403	1408	1406
	MeSH	2.02	1069	1069	1068	1069
	DMS	1.87	819	840	825	828
	DMDS	1.87	114	102	99	105
217	H_2S	1.00	560	557	562	560
	MeSH	1.27	409	405	397	404
	DMS	1.18	328	332	331	330
	DMDS	1.18	49	51	45	48
326	H_2S	0.66	264	273	271	269
	MeSH	0.84	190	192	192	191
	DMS	0.78	148	151	153	151
555	H_2S	0.39	94	92	94	95
	MeSH	0.50	75	65	65	67
	DMS	0.46	45	48	57	50
638	H_2S	0.34	75	74	79	76
	MeSH	0.43	51	44	49	48
882	H_2S	0.24	42	41	41	41

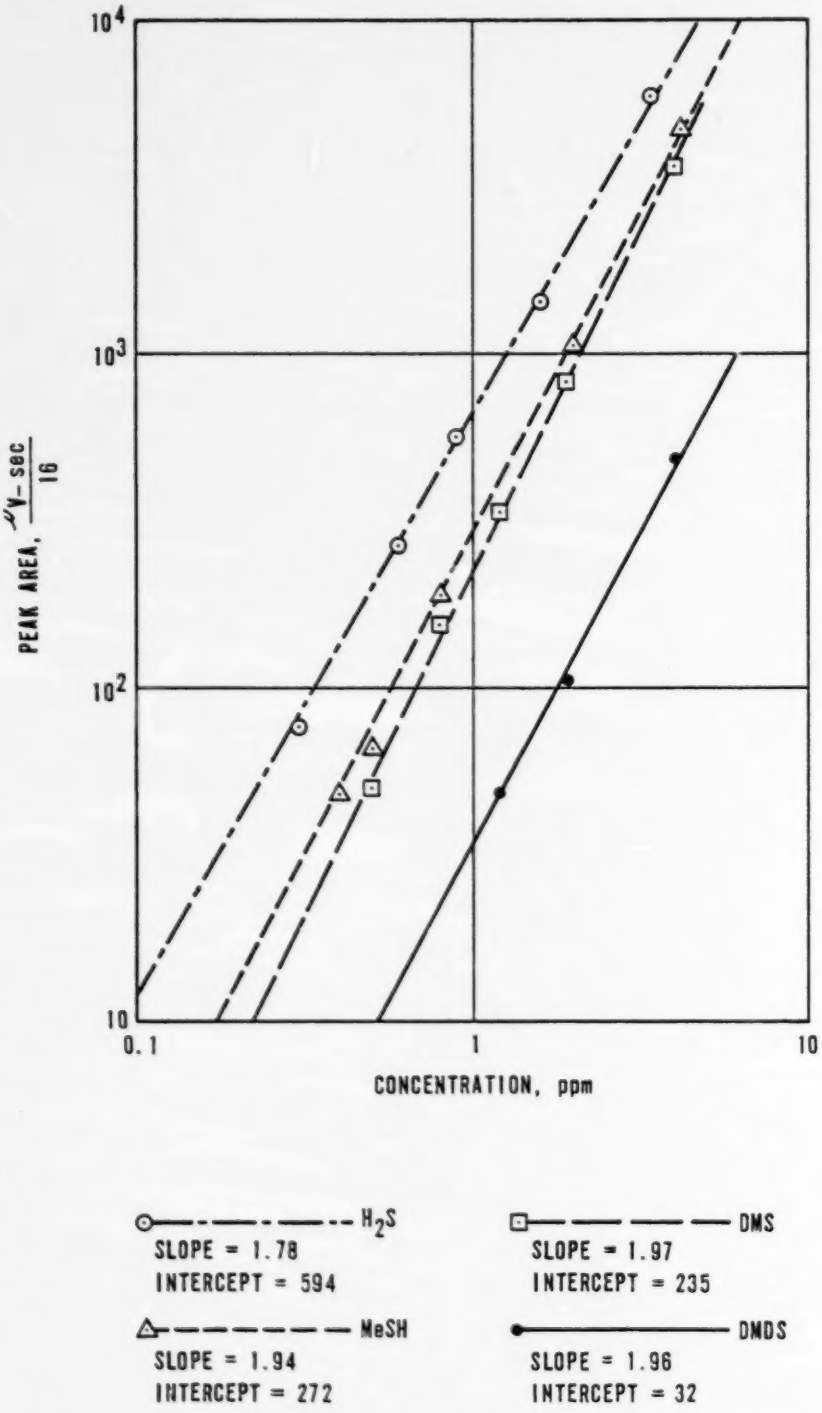


Figure 10. Typical calibration curves for H_2S, MeSH, DMS, and DMDS.

Table 6 shows the stability of the GC system and the output from the Dynacalibrator. The system was set up in a field environment to analyze a gas sample from the permeation tubes every 25 minutes. Alternate values are shown in the table. The poor precision shown in the DMDS response is due to the broad peak. The DMDS peak heights were more precise than the peak areas. No actual data were collected for comparison purposes.

Table 7 presents a comparison of analysis of four cylinders of reduced sulfur gases. These cylinders were purchased from Scott Speciality Gases and analyzed by them prior to shipment. They were analyzed by Hamil and Swynnerton (1) over a period of six months to determine the relative stability of the gases. Their results are shown in column 2 of the table. At the completion of that study, the cylinders were shipped to HE&T for additional analysis. The results of the HE&T testing are shown in column 3 of the table. After completing the analysis, the cylinders were returned to Scott Speciality Gases for an additional analysis (column 4). The analysis by HE&T and Southwest Research Institute (Hamil and Swynnerton) used permeation tubes as a reference. The analysis by Scott used serial dilutions of concentrated mixtures. Considerable variation is observed between the HE&T analysis and that by Southwest Research Institute. The analysis by Scott is much closer to that obtained by HE&T. It was obvious that the lower concentration cylinders (1B and 2B) are not as stable as the more concentrated mixtures. It was also evident that a reduction in the H_2S concentration over a period of fifteen months had taken place. The apparent high results for DMS in all cylinders by HE&T was probably due to the calibration of the permeation tubes.

SYSTEM CALIBRATION AND SAMPLE RECOVERY

One of the most important aspects of the analytical system is to determine the actual calibration factor for the entire system and then to determine if losses of reduced sulfur compounds are taking place within that system. To do this, large volumes of known concentrations of H_2S are required. It is not feasible to use a number of calibrated cylinder gases for this purpose. In order to generate these concentrations of gas on site, a Houston Atlas Inc. Model 601 reference gas generator (HAI 601) was used. Figure 11 shows a schematic drawing of this instrument as modified by HE&T. The instrument is capable of diluting a concentrated gas by a factor of 10^5. The instrument can produce up to 4 liters per minute of a 15 ppm H_2S concentration in air. By changing the injection block volume (see detail A of Figure 11) it was possible to accurately reduce the generated concentration to less than 1 ppm H_2S.

TABLE 6. LONG TERM PRECISION OF REDUCED SULFUR ANALYSES (DAY 1)

Time	H_2S area ($x10^4$ uV-sec) 16	MeSH area ($x10^4$ uV-sec) 16	DMS area ($x10^4$ uV-sec) 16	DMDS area ($x10^3$ uV-sec) 16
0600	1.79	1.35	1.23	1.91
0650	1.84	1.37	1.25	1.30
0740	1.89	1.39	1.27	1.65
0830	1.92	1.40	1.27	1.35
0920	1.97	1.41	1.28	1.08
1010	2.00	1.42	1.29	1.32
1100	2.06	1.44	1.32	1.37
1150	2.04	1.41	1.25	1.19
1305	2.18	1.49	1.34	0.91
1355	2.17	1.48	1.35	1.49
1445	2.16	1.49	1.32	1.10
1535	2.17	1.49	1.33	1.08
1625	2.16	1.49	1.33	1.14
1715	2.16	1.49	1.35	0.87
1805	2.18	1.49	1.34	0.72
$\bar{X}$	2.05	1.44	1.30	1.23
Std Dev	±0.14	±0.05	±0.41	±0.31
Std Dev (%)	6.8	3.5	3.1	24.9
Concentrations ppm	4.7	5.9	5.5	5.5

TABLE 6 (CONTINUED). LONG TERM PRECISION OF REDUCED SULFUR ANALYSES (DAY 2)

TIME	H_2S area ($\times 10^4$ uV-sec) 16	MeSH area ($\times 10^4$ uV-sec) 16	DMS area ($\times 10^4$ uV-sec) 16	DMDS area ($\times 10^3$ uV-sec) 16
0930	1.95	1.26	1.07	0.79
1000	2.07	1.31	1.10	0.54
1030	2.11	1.50	1.25	0.88
1100	2.09	1.38	1.18	0.66
1130	2.07	1.38	1.15	0.69
1200	2.06	1.39	1.35	1.92
1230	2.10	1.46	1.35	2.05
1300	2.11	1.46	1.27	1.91
1330	1.95	1.40	1.18	1.57
1400	2.00	1.42	1.21	0.84
1430	2.03	1.45	1.27	0.80
1500	2.05	1.51	1.25	1.40
1530	2.06	1.58	1.39	1.39
1600	2.05	1.68	1.46	1.31
1630	2.02	1.72	1.37	1.19
1700	2.02	1.61	1.46	1.66
1730	1.99	1.62	1.43	0.98
1800	1.98	1.51	1.14	1.94
1900	1.97	1.53	1.27	2.37
1950	1.79	1.54	1.14	1.63
2040	1.81	1.53	1.06	1.96
$\bar{X}$	2.01	1.47	1.25	1.36
Std Dev	±0.08	±0.14	±0.12	0.55
Std Dev (%)	±4.2	±0.4	9.6	40.4
Concentrations ppm	4.7	5.9	5.5	5.5

TABLE 7. COMPARISON OF REDUCED SULFUR CONCENTRATION IN CYLINDERS MEASURED BY DIFFERENT LABORATORIES

Cylinder identification	Compound	3 Conc HE&T+ (ppm)	1 Conc Scott± (ppm)	2 Conc SwRI* (ppm)	4 Conc Scott** (ppm)
4B	H_2S	5.47	5.84	3.32	5.09
	MeSH	10.71	9.99	6.68	10.38
	DMDS	6.43	5.52	4.5	7.98
3B	H_2S	4.07	4.00	2.46	3.79
	MeSH	7.35	6.01	4.45	7.07
	DMS	6.48	4.76	4.55	5.39
	DMDS	2.86	2.83	3.25	4.11
2B	H_2S	0.29	0.925	0.25	0.290
	MeSH	1.50	1.96	1.23	1.67
	DMS	2.36	1.93	1.95	1.98
	DMDS	1.36	1.38	2.50	2.04
1B	H_2S	0.14	0.742	<0.1	0.084
	MeSH	0.81	0.574	0.65	0.888
	DMS	0.54	0.430	0.45	0.507
	DMDS	1.00	0.866	----	0.805

\+ Analyzed by HE&T on 3/4/80
± Analyzed by Scott prior to shipment 12/78
* Analyzed by SwRI on 6/4/79
** Analyzed by Scott on 6/10/80

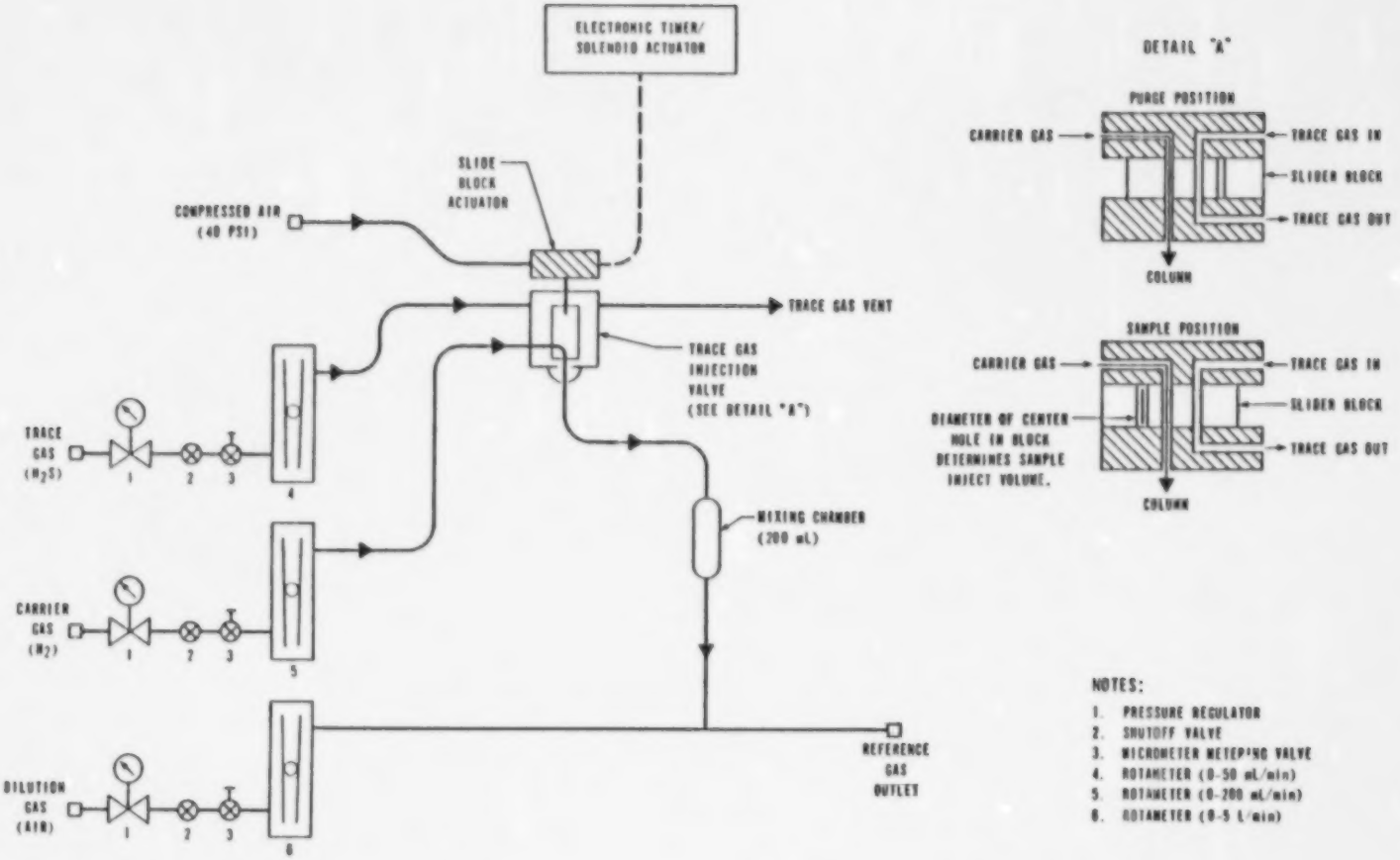


Figure 11. Schematic drawing of Houston Atlas, Inc. Model 601 (HAI 601) reference gas generator.

Figure 12 shows the performance of the HAI 601 in accurately generating known concentrations of the standard gas. The figure primarily illustrates the stability of the instrument to generate the concentrations over a long period of time. The initial low response was not from the HAI 601 but from the GC system. At time zero the HAI 601 and the GC were started. A considerable amount of time (2 hours) was required for the GC to stabilize initially. This fact is indicated by the graph. After that initial period the output from the 601 and the GC response is extremely stable.

Secondly, Figure 12 shows the rapidity with which the H_2S concentration changed after the injection rate was changed on the HAI 601. Normally five minutes were required for this change in concentration. This time period represents two injections on the GC at approximately three minutes apart. Further, the figure demonstrates the calibration curve and the calibration data generated by simply changing the injection rate. The calibration data show that the measured concentration from the calibration curve was always extremely close to the calculated concentration. By accurately measuring the flow through the HAI 601 and the injection rate of the trace gas, a linear output concentration over a range of more than one hundred fold was produced.

The performance of the HAI 601 made it possible to generate, for instance, a five ppm concentration to go directly to the GC for calibration. The injection rate was then changed to generate a 50 ppm concentration used to check the dilution factor of the dilution unit. It was also possible to generate large volumes of low concentration gas to check recovery throughout the entire system.

It was possible to calculate the desired output concentration within plus or minus fifteen percent. To determine the actual output from the HAI 601 at a given injection rate and gas flow rate, it was necessary to direct the gas directly to the GC and determine the concentration based on a permeation tube generated calibration curve. This calibration was necessary since the injector block (see detail A Figure 11) has a known diameter hole through the block which will inject a known volume of gas. The holes in the injector block are of a nominal value. For instance, a nominal 10 uL hole was 12.2 uL based on repeated calibrations with the slider block. Since a number of different diameter holes are available from the manufacturer, it is necessary to calibrate each slider block upon arrival. This instrument was not capable of generating reference gas without calibration relative to another standard.

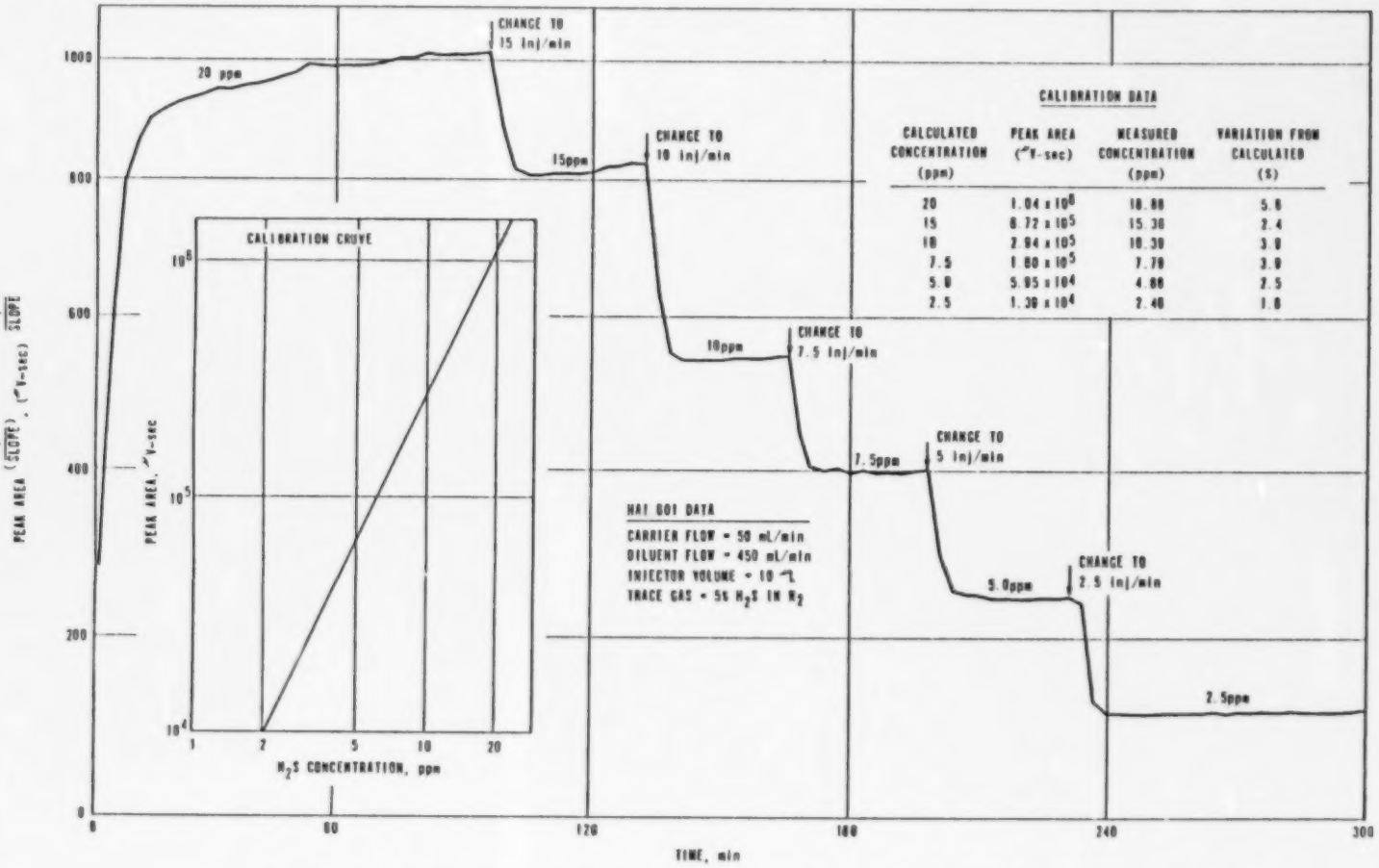


Figure 12. Performance of Houston Atlas, Inc. Model 601 (HAI 601) reference gas generator to deliver known concentrations of standard gas.

SECTION 5

FIELD EVALUATION

At the completion of the laboratory evaluation of all the equipment in the system, a field evaluation was conducted to determine the applicability of the system for analyzing reduced sulfur compounds at kraft pulp mills. Sixteen days were spent in the field. A recovery boiler, smelt dissolving tank vent, and a lime kiln were tested. The object of the field evaluation was not to determine the emissions from the sources, but, instead, to determine if the method could be used to conduct emission testing over a period of time.

Due to construction activities at the mill, it was not possible to test all sources during a given field trip. Three different trips were required to test all sources and to complete the evaluation. During the first field trip, a lime kiln was to be tested. It was discovered that some interference due to CO_2 was still present in the analysis. At the completion of the field evaluation, the GC conditions were changed slightly to give better separation of CO_2 and H_2S and the lime kiln was tested again during one of the later field trips.

Table 8 shows the recovery of H_2S obtained through the analytical system before, during, and after sampling. Throughout the testing a filter was placed on the end of the probe to detect losses. The poorest recoveries were obtained after sampling on the lime kiln. In each case, it was possible to sample for more than eight hours on a given source using the same impinger scrubbing solution without cleaning the system, and still obtain reasonable recoveries of H_2S through the system. Through a series of experiments, better recoveries could be obtained when using high concentrations of H_2S. The recovery of H_2S through the system was checked by putting an excess of a known concentration of H_2S either before or after the filter while the system was operating normally. The excess reference gas would simply be vented to the atmosphere rather than drawn through.

Table 9 shows the analysis of the emissions from the lime kiln on a day when COS was present in the emission. Throughout the day the pulp mill operators were changing the concentration of the oxygen being introduced into the lime kiln. This change in concentration correlates with the TRS concentration being emitted, as would be expected. The important thing to note from this table is that significant amounts of COS were being emitted.

TABLE 8. H_2S RECOVERY THROUGH THE ANALYTICAL SYSTEM

Source	H_2S Conc (ppm)	Timing	Point of H_2S insertion	System recovery (%)
Lime	4.6	Before sampling	Upstream of filter	93
Kiln	4.6	Before sampling	Downstream of filter	100
	4.6	After sampling 4.3 hrs.	Upstream of filter	96
	4.6	After sampling 4.3 hrs.	Downstream of filter	102
	4.9	Before sampling	Upstream of filter	100
	4.9	After sampling 3.3 hrs.	Downstream of filter	78
	4.9	After sampling 6.7 hrs.	Downstream of filter	80
	4.7	After sampling 6.7 hrs.	Upstream of filter	77
	15.6	After sampling 10.5 hrs.	Upstream of filter	82
Smelt	6.2	Before sampling	Upstream of filter	87
Tank	5.6	After sampling 10.0 hrs.	Upstream of filter	84
Vent	6.2	Before sampling	Upstream of filter	95
	5.6	After sampling 10.0 hrs.	Upstream of filter	95
	6.5	Before sampling	Upstream of filter	93
	6.5	After sampling 3.0 hrs.	Upstream of filter	92
Recovery	4.9	Before sampling		96
Boiler	4.9	After sampling 4.0 hrs.	Downstream of filter	92
	4.9	After sampling 4.0 hrs.	Upstream of filter	90
	5.7	Before sampling	Downstream of filter	100
	6.2	After sampling 8.0 hrs.	Upstream of filter	103
	6.2	After sampling	Downstream of filter	105

TABLE 9. ANALYSIS OF LIME KILN EMISSIONS

Time	H_2S concentration (ppm)	COS* concentration (ppm)
Day 1		
1507	2.3	3.7
1514	3.0	4.7
1528	3.8	4.4
1535	5.1	5.3
1542	8.7	6.4
1549	8.1	6.4
1556	7.8	6.8
1603	8.6	7.9
1610	18.9	10.0
1617	35.9	14.1
1624	24.3	13.3
1631	11.5	11.9
1638	7.9	9.9
1645	13.9	10.0
1652	25.3	15.0
1659	37.0	15.0
1706	26.9	13.8
1713	11.5	8.9
1720	5.8	6.6

* No calibration curve was available for COS and the apparent concentrations were determined using the H_2S calibration curve. The COS was identified by retention time.

Table 10 shows a comparison of TRS analysis by GC and by coulometric titrator. On this day, H_2S was not observed being emitted from the stack. During this one and one half hour period COS was all that was observed being emitted and, as would be expected, the coulometric titrator was reading this COS as total reduced sulfur. The COS concentration measured by the GC was determined by plotting the COS peak areas on the H_2S calibration curve. This will not give the exact concentration of COS but it is within 20 percent of the actual concentration since the retention times of the compounds are near the same and both contain one sulfur atom.

Tables 11 and 12 show some example TRS data collected on a recovery boiler and a smelt dissolving tank vent, respectively. The data were collected during an actual emission test and the tables show an example format of the data. The system correction factor was extremely constant in each case. It should be noted that in Table 12, two smelt dissolving tank vents were being tested simultaneously. Two separate trains were being used for the testing. The train used on the east side was new and had not been properly conditioned. The system correction factor was higher in that system due to losses of H_2S within the system.

Tables 13 and 14 show the system correction factors and the recoveries of H_2S through the system after sampling the recovery boiler and the smelt dissolving tanks. In Table 13 the sampling system was well conditioned and had been used for several tests. Note the excellent recoveries obtained throughout the day. Table 14 shows the effect of using a new system for the sampling. Note that the recoveries obtained with the new system (the east side) were not quite as good as those obtained for the conditioned system on the west side. It should still be noted that the system correction factor for both systems, the new and the old, was constant throughout the sampling.

During the field testing one of the objectives was to evaluate the use of a Tracor Model 560 Gas Chromatograph with a Hall Electrolytic Detector. The instrument was supplied by Tracor Instruments, but when it arrived at HE&T it was not operational. After a serviceman repaired the instrument, it was found that, due to the heavy current requirements of the instrument, it might not always be possible to supply enough current for the instrument to properly operate in a field environment. When the instrument was transported to the pulp mill for the field evaluation, a separate circuit was established for the instrument. Twenty amps of current were available for use on that circuit. Considerable time was spent with the instrument to get it operational, but a signal response could not be obtained with the detector. After two days of work, the efforts to make the instrument operational were discontinued.

TABLE 10. COMPARISON OF TRS ANALYSES BY GC AND COULOMETRIC TITRATOR ON A LIME KILN

Time	TRS concentration+ (ppm)	COS** concentration* (ppm)
Day 2		
1430	26.1	21.4
1435	29.3	25.8
1440	29.3	27.2
1445	29.3	28.4
1450	30.1	32.1
1455	32.5	32.1
1500	33.5	32.1
1505	32.5	28.4
Mean	30.3	28.4
RSD (%)	7.9	14.2

+ The TRS concentration was measured with a Barton Coulometric Titrator. Instrument was operated in parallel with GC. The same SO_2 scrubber and sample line were used for both instruments.

* The COS concentration was determined by GC. The concentrations were calculated using a calibration curve for H_2S. H_2S concentration was less than 1 ppm during the comparison.

** The COS was identified by retention time.

TABLE 11. EXAMPLE TRS DATA - RECOVERY BOILER

	Run number 1		Run number 2		Run number 3	
Start time	1115		1627		2014	
Stop time	1452		1930		2318	
Injection number	H_2S (ppm)	CH_3SH (ppm)	H_2S (ppm)	CH_3SH (ppm)	H_2S (ppm)	CH_3SH (ppm)
1	2.38	1.06	2.86	1.17	2.99	1.40
2	2.47	1.23	2.50	1.18	2.92	1.25
3	2.78	1.21	2.90	1.41	3.17	1.38
4	2.19	0.93	3.13	1.41	2.36	1.12
5	2.40	1.05	2.87	1.62	2.75	1.14
6	2.98	1.24	2.36	1.17	2.79	1.36
7	2.35	1.35	2.47	1.26	3.28	1.33
8	2.39	1.20	2.23	1.08	3.00	1.23
9	3.59	1.30	2.69	1.12	2.30	0.91
10	2.94	1.31	2.26	1.10	1.93	0.77
11	3.03	1.33	2.42	0.88	2.03	1.06
12	3.55	1.49	2.80	1.17	2.19	1.38
13	2.57	1.10	2.16	0.91	2.50	0.95
14	2.29	1.18	2.48	0.95	2.36	0.99
15	2.64	1.32	2.34	1.00	1.79	1.27
16	2.61	0.97	2.81	1.11	2.23	0.87
17	3.04	1.14	1.95	0.77	1.89	0.79
18	2.65	1.12	1.95	0.83	2.49	1.11
19			2.01	0.89	2.27	0.95
20			2.18	0.95	1.83	0.76
Mean	2.71	1.20	2.47	1.10	2.45	1.10
System correction factor	1.39	1.39	1.35	1.35	1.39	1.39
Corrected conc	3.77	1.67	3.33	1.49	3.41	1.93
TRS	5.43		4.82		5.34	
Oxygen conc (%)	5.7		5.4		6.0	
TRS corrected to 8% O_2	4.6		4.0		4.6	

Concentrations must be corrected by the system correction factor for each run.
System correction factor includes all system TRS losses.
DMS and DMDS were below the detectable limit of 0.5 ppm.

TABLE 12. EXAMPLE TRS* DATA - SMELT DISSOLVING TANK VENTS

	Run number 1		Run number 2		Run number 3	
	East	West	East	West	East	West
Start time	1005	1020	1305	1320	1640	1650
Stop time	1305	1320	1628	1650	1940	2000
Injection number	H_2S (ppm)	H_2S (ppm)	H_2S (ppm)	H_2S (ppm)	H_2S (ppm)	H_2S (ppm)
1	0.47	1.41	0.52	0.33	0.74	0.89
2	0.46	0.35	0.54	0.35	0.76	0.81
3	0.46	0.41	0.51	0.44	0.71	<0.33
4	0.47	0.41	0.67	0.42	0.51	<0.33
5	0.46	0.33	0.67	0.35	0.49	0.41
6	0.49	0.41	0.81	0.45	0.51	0.40
7	0.49	0.40	0.80	0.45	0.53	0.43
8	0.47	0.33	0.81	0.36	0.53	0.44
9	0.47	<0.33	0.83	<0.33	0.49	0.34
10	0.41	<0.33	0.85	0.48	0.43	<0.33
11	0.34	<0.33	0.91	0.73	0.50	0.33
12	0.47	<0.33	0.96	0.71	0.65	<0.33
13	0.47	0.33	0.89	0.93	0.61	<0.33
14	0.71	<0.33	0.90	0.75	0.72	<0.33
15	0.70	<0.33	0.82	0.72	0.74	<0.33
16	0.78	<0.33	0.81	0.89	0.82	<0.33
17		0.38			0.88	<0.33
18		<0.33			1.03	<0.33
19		<0.33				0.71
20						0.78
21						0.94
22						1.09
23						1.31
24						1.27
25						1.13
26						1.02
Mean	0.51	0.35	0.77	0.54	0.65	0.60
System+ correction	1.37	1.20	1.44	1.30	1.44	1.28
Corrected conc (ppm)	0.70	0.42	1.11	0.62	0.94	0.77
Average conc (ppm)	5.66		0.86		0.86	

+ System correction factor includes all TRS losses throughout the system.
* All concentrations are H_2S, no other reduced sulfur compounds were detected.

TABLE 13. TRS SYSTEM CORRECTION FACTORS AND SYSTEM RECOVERIES - RECOVERY BOILER

Time	Measured GC conc	Dilution box		Complete system		Recovery (%)
		Measured conc	Correction factor	Measured conc	Correction factor	
1015	5.39	3.62	1.49	3.70	1.46	102
1245	--	--	--	--	--	--
1620	--	--	--	4.08	1.39	87
1940	--	--	--	4.21	1.35	90
2116	--	4.67	1.21	--	--	--
2130	5.67	--	--	--	--	--
2320	--	4.75	1.25	--	--	--
2340	--	--	--	4.30	1.39	91
2355	5.96	--	--	--	--	--

TABLE 14. TRS SYSTEM CORRECTION FACTORS AND SYSTEM RECOVERIES - SMELT DISSOLVING TANK VENTS

Time	Measured GC conc	Dilution box Measured conc	Dilution box Correction factor	East side Measured conc	East side Correction factor	East side Recovery (%)	West side Measured conc	West side Correction factor	West side Recovery (%)
0915	--	--	--	4.50	1.37	87	--	--	--
0925	--	5.19	1.19	--	--	--	--	--	--
0940	6.16	--	--	--	--	--	--	--	--
0955	--	--	--	--	--	--	4.91	1.25	95
1335	--	--	--	4.29	1.37	89	--	--	--
1400	--	4.82	1.22	--	--	--	--	--	--
1415	--	--	--	--	--	--	4.88	1.20	102
1420	5.88	--	--	--	--	--	--	--	--
1700	--	--	--	3.87	1.44	78	--	--	--
1710	--	4.93	1.13	--	--	--	--	--	--
1720	5.57	--	--	--	--	--	--	--	--
1730	--	--	--	--	--	--	4.28	1.30	87
2002	--	--	--	3.87	1.44	84	--	--	--
2018	--	--	--	--	--	--	4.37	1.28	95
2032	--	4.61	1.21	--	--	--	--	--	--
2040	5.59	--	--	--	--	--	--	--	--

The completion of the field evaluation of Method 16 indicated several important things about total reduced sulfur emission testing. The most important of these are listed below.

1. It was necessary to maintain the gas chromatograph, dilution system, and calibration system in a relatively stable environment. Large temperature changes would cause fluctuation in the output of the calibration gas and drift within the gas chromatograph.

2. Significant losses of H_2S were not observed in the system after it had been sampling for significant times. It should be possible to use this system to perform three runs on a given source without changing the scrubber solution or without cleaning the system.

3. By reducing the gas temperature at the source, it was not necessary to use a heated sample system or to dilute the sample gas with air to reduce the dew point. This enables a more sensitive analysis to take place without the added error of a dilution system.

4. The SO_2 scrubbing solution proved effective in removing SO_2 without affecting the other reduced sulfur compounds.

5. The modified system was shown to meet the EPA source testing criteria.

REFERENCES

1. Hamil, H.F. and N.F. Swynnerton. A Study to Improve EPA Methods 15 and 16 for Reduced Sulfur Compounds. EPA Contract No. 68-02-2489 Final Report, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, accepted for publication.

2. The National Council of the Paper Industry for Air and Stream Improvement, Incorporated. A Study of Alternate SO_2 Scrubber Designs Used for TRS Monitoring. Special Report 77-05, New York, New York.

APPENDIX A

PROPOSED METHOD 16. SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

Introduction

The method described below uses the principle of gas chromatographic separation and flame photometric detection. Since there are many systems or sets of operating conditions that represent usable method of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used provided that the criteria set below are met.

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the emission source and bubbled through a cold citrate buffer scrubbing solution to reduce SO_2, particulate matter and moisture. An aliquot of the dry sample is then analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability. This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns and smelt dissolving tank vents at kraft pulp mills.

2. Range and Sensitivity

2.1 Range. Coupled with a gas chromatographic system utilizing a one milliliter sample size, the linear range of the FPD for each sulfur compound is approximately 0.5 to 25 ppm. The upper limit may be expanded by dilution of the sample gas before analysis or by the analysis of a smaller sample. Kraft mills normally have TRS concentraion in the linear range of the calibration curve.

For sources with emission levels between 20 and 200 ppm, the measuring range can be best extended by reducing the sample size or diluting the sample before analysis or both.

2.2 Sensitivity. Using a 0.3 mL sample size, the minimum detectable concentration is less than 0.5 ppm for each reduced sulfur compound.

3. Interferences

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by reducing the sample gas temperature to less than 5°C at the source with the cold scrubbing solution. Heated sample lines may be necessary in cold climates to prevent condensation if the ambient temperature is less than 5°C.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effect on the flame photometric detector. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of Section 4.1.

3.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system and by adsorbing reduced sulfur compounds. This interference may be eliminated by the use of a probe filter.

3.4 Sulfur Dioxide. SO_2 is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from other compounds of interest by the GC system. The procedure must be designed to eliminate this problem either by the choice of separation columns or by removal of SO_2 from the sample. Sulfur dioxide may be removed by a citrate buffer solution at the source.

Compliance with this section can be demonstrated by submitting chromatograms of calibration gases with SO_2 present in the same quantities expected from the emission source to be tested. Acceptable systems shall show baseline separation with the amplifier attenuation set so that the reduced sulfur compound of concern is at least 50 percent of full scale. Baseline separation is defined as a return to zero $\pm$10 percent in the interval between peaks.

3.5 Carbonyl Sulfide. The presence of COS has been demonstrated in some TRS emission sources at kraft pulp mills. Since COS is not included in TRS calculations, it may be desirable to separate it from the four reduced sulfur compounds defined as TRS. COS separation may be achieved through the use of the appropriate GC column(s).

4. Precision and Accuracy

4.1 GC/FPD and Dilution System Calibration Precision. A series of three consecutive injections of the same calibration gas at a concentration in the linear range of the instrument shall produce results (peak heights or peak areas) for which the standard deviation does not exceed 10 percent of the mean of the injections.

4.2 GC/FPD and Dilution System Calibration Linearity. A series of at least four concentrations will be used to prepare a calibration curve. After preparation of the calibration curve, it will be used to calculate the concentration of the calibration gas at each point from the average GC response to each gas. The absolute mean of the relative difference between the known concentration and the calculated concentration will not exceed 0.1 when calculated by the equation below:

$$RD = \frac{1}{N}\sum\frac{|KC_i - CC_i|}{KC_i}$$

where:

RD = relative difference
N = number of calibration points
KC_i = known concentration of the ith calibration gas
CC_i = calculated concentration of ith calibration gas

4.3 GC/FPD and Dilution System Calibration Drift. The calibration drift will be determined by the analysis of a reference mixture of one or more of the reduced sulfur compounds. The reference gas concentration will be within the range of the concentration observed at the source. The calculated concentration of the mean of three injections made at the beginning and at the end of any 8 hour period shall not differ by more than $\pm$10 percent.

4.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

4.5 Minimum Detection Limit. The minimum detectable concentration for each of the reduced sulfur compounds should be $\leq$10 percent of the applicable TRS standard.

5. *Apparatus* (see Figure 16-1)

5.1 Sampling

5.1.1 Probe. The probe liner must be made of inert material such as Teflon. It should be designed to incorporate a filter and allow calibration gas to enter the probe immediately downstream of the filter assembly. Any portion of the probe not exposed to the stack gas must be heated or insulated to prevent moisture condensation.

5.1.2 SO_2 Scrubbers. The impingers in the scrubber system must be constructed from an inert material such as Teflon. It should be designed to allow maximum gas to solution contact without causing excessive pressure drop. Solution volume and dead volume within the impingers should be minimized to reduce delay time from sample collection to analysis. The scrubbers must be immersed in an ice bath (or equivalent).

5.1.3 Sample Line. The sample line must be made of Teflon (or other inert material), no greater than 1.3 cm (1/2") inside diameter. It may be heated if the likelyhood of moisture condensation exists.

5.1.4 Sample Pump. The sample pump shall be a leakless diaphragm type or equivalent. It must be capable of drawing 4 L/min of a vacuum of 120 mm Hg.

5.2 Dilution System. If a dilution system is used, it must be constructed such that all sample contacts are made of inert materials (e.g., stainless steel or Teflon). It must be capable of approximately a 1:10 dilution of the sample.

The vacuum or pressure within the unit must be monitored to an accuracy of ± 5 percent by a manometer or other calibrated gauge.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column, valves, and connecting tubing at the proper operating temperature $\pm 1^{\circ}C$.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature $\pm 1^{\circ}C$.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector. FPD must be equipped with a 394 nm filter to make it sulfur specific.

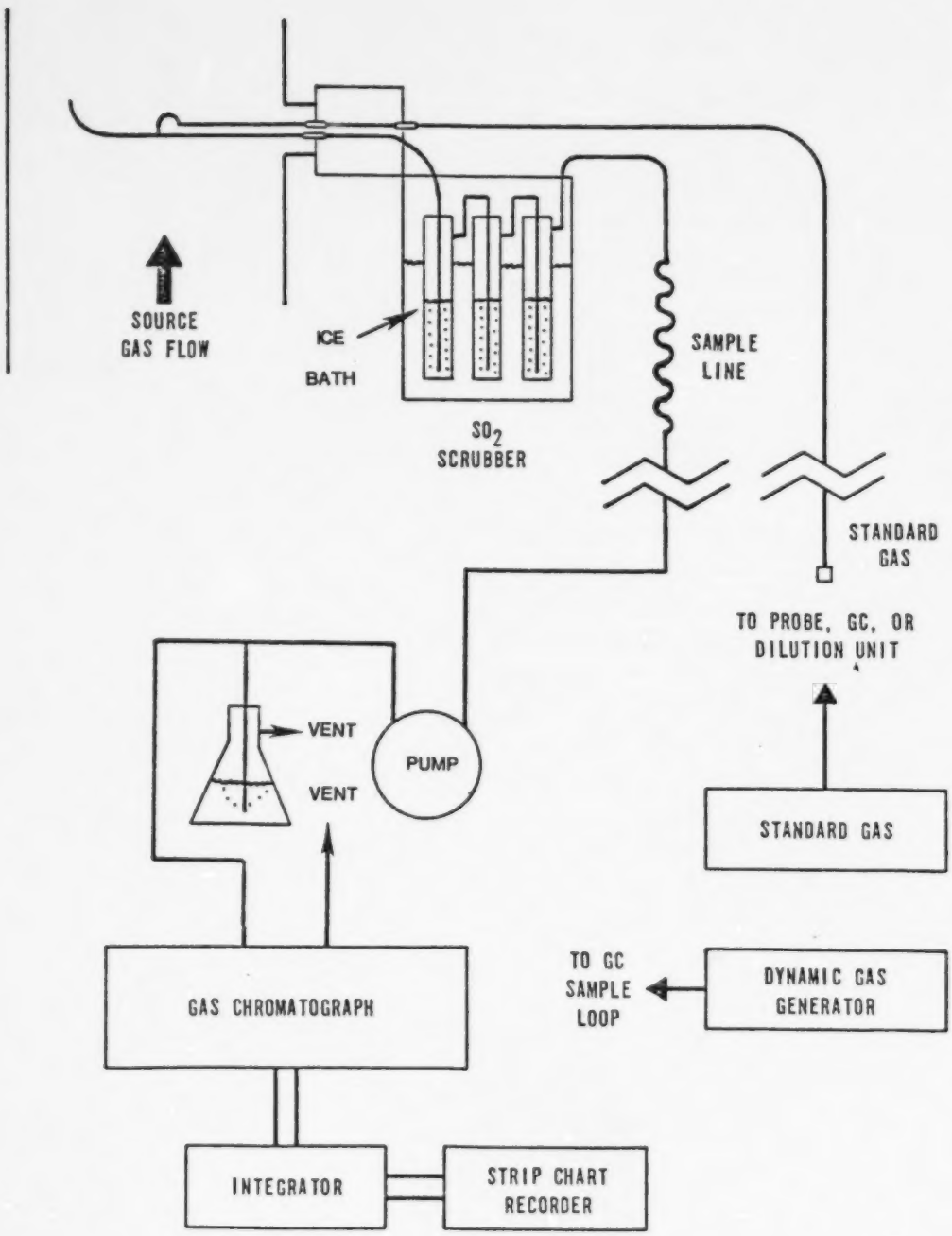


Figure 16-1. Schematic Drawing of TRS Analytical System

5.3.5 Recorder and/or Integrator. Compatible with the output voltage range of the electrometer.

5.4 Gas Chromatograph Columns. The GC column system must be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS and DMDS. It must also demonstrate freedom from known interferences defined in Section 3.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as baseline separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined in Section 3.4. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5 Calibration System. The calibration will make use of Teflon permeation tubes containing the following components:

5.5.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.5.2 Flow System. To maintain constant inert gas flow ($\pm$2%) over permeation tubes. The gas flow rate will be measured at each time of use to determine the concentrations. The flow will be measured with a soap bubble flow tube certified accurate ($\pm$2 percent). The proper size flowmeter will be selected such that the flow will be measured over a 10-20 second time period.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within $\pm 0.1^{\circ}C$. The gas will be heated to the same temperature prior to entry into the permeation tube chamber.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within $\pm 1^{\circ}C$.

5.5.5 Permeation Tubes. Teflon permeation tubes with gravimetrically certified emission rates. Emission rates must be determined within $\pm$5 percent by a minimum of four weighings at the same temperature used for instrument calibration.

5.5.6 Constant Head Device. Device capable of maintaining constant flow and constant pressure within the GC sample loop during calibration regardless of gas flow across permeation tubes.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research grade or better.

6.3 Carrier Gas. Perpurified grade or better.

6.4 Diluent. Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons. Dilute gas injected into the GC under the most sensitive conditions should not give a response for any of the reduced sulfur compounds.

6.5 Calibration Gases. Permeation devices, one each of H_2S, MeSH, DMS and DMDS, gravimetrically calibrated and certified at some convenient operating temperature are the primary reference. Cylinders of accurately known concentration may be used for calibration, recovery studies and other uses requiring high flow conditions may be used if the cylinder concentration is related to permeation tubes immediately after use. Other methods of generating reference gas may be used if the concentration is related to permeation tube standards.

6.6 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water (284 grams of sodium citrate may be substituted for the potassium citrate). The pH must be adjusted to 5.5 - 5.6 with citric acid or potassium citrate as required.

7. Pretest Procedures

After the complete measurement system has been set up at the site and deemed operational, the following procedures should be completed before sampling is initiated.

7.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. All components of the sample train upstream of the vacuum pump can be checked by capping the sample inlet at the source observing a rotameter downstream of the pump while the system is under a vacuum of 120 mm Hg or more. The leak rate must be less than 1% of the sampling rate.

Alternatively, the following procedure may be used: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 120 mm Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, the components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters, of the GC output, of changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component, or if the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8. Calibration

Prior to any sampling run, calibrate the gas chromatograph system using the following procedures. (If more than one run is performed during any 24 hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24 hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within $\pm 0.1^{\circ}C$. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1 hour intervals. The permeation tubes can be assumed to have reached equilibrium when the results of consecutive hourly samples agree within ± 15 percent.

Vary the amount of gas flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The gas flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K \frac{P_r}{ML}$$

where:

C = Concentration of permeant produced in ppm.
P_r = Permeation rate of the tube in ug/min.
M = Molecular weight of the permeant (g/g-mole).
L = Flow rate, L/min, of gas over permeant @ 20°C, 760 mm Hg.
K = Gas constant at 20°C and 760 mm Hg = 24.04 L/g mole.

8.3 Calibration of analysis system. Generate a series of four or more known concentrations spanning the linear range of the FPD for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in Section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration curves. Use a log-log linear least squares best fit of the data to the equation:

$$Y = aX^b$$

where:

Y = peak height or peak area
X = concentration of compound
a = intercept
b = slope of curve

Alternatively, plot the peak height or peak area versus the causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. The calibration curve will be the straight line that best fits the points.

8.5 Calibration of Dilution System. If a dilution system is used, generate a known concentration of hydrogen sulfide with a flow rate greater than the flow requirement of the dilution system. Adjust the flow rate of diluent gas for the first dilution stage so that the desired level of dilution is approximated. Adjust all sample flows and vacuums within the dilution system such that they are at the same conditions as when sample is collected from the source.

Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in Section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required.

8.6 Sample System loss. A known concentration of hydrogen sulfide at the level of the applicable standard, $\pm$20 percent, must be introduced into the sampling system in sufficient quantities to insure that there is an excess of sample which must be vented to the atmosphere. The sample must be introduced immediately after the probe and filter and transported through the remainder of the sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss.

9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution gas enters the stack through the port. Begin sampling and condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Source gas is drawn through the sampling system at the rate of 1-2 L/min. A small portion of the gas is diluted (if required) and continuously passed through the GC sample loop. Periodic injections are made into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of a minimum of 16 individual analyses (injects) performed over a period of not less than 2 hours nor more than 6 hours. Time between injections must be equally spaced during the sampling period such that no more than 8 data points are collected during any one hour period.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. Post-Test Procedures

10.1 Sample System Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system in sufficient quantities to insure that there is an excess of sample which must be vented to the atmosphere. The sample must be introduced immediately after the probe and filter and transported through the remainder of the sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. Since H_2S is more reactive than the other reduced sulfur compounds, the measured sampling system loss is a "worst case" and can be applied directly to all compounds.

For sampling losses greater than 20 percent in a sample run, the sample run is not to be used when determining the arithmetic mean of the performance test. For sampling losses of 0-20 percent, the sample concentration must be corrected by multiplying the measured concentration by the system correction factor. This factor includes correction for moisture in the sample, sample line losses, losses in the scrubber and any dilution of the sample gas.

The known gas concentration may be generated using permeation tubes, cylinders of H_2S mixed in air or other methods of preparing H_2S on site as long as all concentrations are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24 hour period, perform a partial recalibration using the procedures in Section 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.2. The calibration drift should not exceed the limits set forth in Section 4.2. If the drift exceeds this limit, the intervening run or runs should be considered invalid. The tester however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

11.1 Determine the concentration of each reduced sulfur compound detected directly from the calibration curves or the concentrations may be calculated using the equation for the least square line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$TRS = \Sigma \frac{(H_2S,\ MeSH,\ DMS,\ 2DMDS)}{SCF}$$

where:

TRS = Total reduced sulfur in ppm, dry basis
H_2S = Hydrogen sulfide, ppm (measured)
MeSH = Methyl mercaptan, ppm (measured)
DMS = Dimethyl sulfide, ppm (measured)
DMDS = Dimethyl disulfide, ppm (measured)
SCF = System correction factor (dimensionless)

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \frac{\Sigma\ TRS_i}{N}$$

where:

Average TRS = Average total reduced sulfur in ppm, dry basis
TRS = Total reduced sulfur in ppm as determined in Section 11.2
N = Number of samples

11.4 Average Concentration of individual reduced sulfur compounds.

$$C = \frac{\Sigma\ S_i}{N}$$

where:

S_i = Concentration of any reduced sulfur compound from the ith sample injection, ppm
C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm
N = Number of injections in any run period

11.5 Calculation of System Correction Factors.

$$SCF = \frac{[H_2S]\ probe}{[H_2S]_{GC}}$$

where:

SCF = System correction factor, dimensionless
$\{H_2S\}$ probe = H_2S concentration put in at probe, ppm
$\{H_2S\}_{GC}$ = H_2S concentration measured at GC (from calibration curve), ppm

11.6 Calculation of Sample System Loss.

$$SSL = [1 - SCF] \times 100\%$$

where:

SSL = sample system loss